**ÇUKUROVA UNIVERSITY**
**INSTITUTE OF NATURAL AND APPLIED SCIENCES**

**MSc THESIS**

**Mohamad AL CHEIKH MOHAMAD AHMAD**

# USE OF ETHYL ALCOHOL AS A REDUCTANT AGENT IN A SCR SYSTEM AT LOW TEMPERATURES

**DEPARTMENT OF AUTOMOTIVE ENGINEERING**

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 04/01/2019

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## ABSTRACT

## MSc THESIS

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In this study, Ag / Cu based catalyst was synthesized with the impregnation method for hydrocarbon-selective catalytic reduction (HC-SCR) system. In this system, a mixture of ethyl alcohol and distilled water was used as a reducing agent and the effect of the synthesized catalyst on $NO_x$ conversion efficiency was investigated.The analysis done by SEM, XRD, and BET revealed the structural and chemical peoperties of the catalysts. In the SCR exhaust test performance system, experiments in a temperature ranging from 170°C to 260°C, and 2 different space velocities SV(20000$h^{-1}$, and 40000$h^{-1}$) were conducted using the prepared catalyst. The tests were conducted using a 2 cylinders, V-type diesel motor with constant speed(3000r/m), and in 4 different engine loads(1,2,3, and 4KW). These tests determined the effects of SCR catalyst over $NO_x$ emissions rate. In colclusion, $NO_x$ converison rates changed approximately between 55% and 65%. The highest $NO_x$ conversion rate recorded in the tests was approximately 68% at 4KW engine load, 100% ehtyl alcohol spraying, and SV=20000$h^{-1}$.



**Keywords:** NOx, SCR, exhaust emission, Reductants, Diesel motor

# ÖZ

## YÜKSEK LİSANS TEZI

**SCR SISTEMINDE ETYL AKOL INDIRGEYICI OLARAK DÜŞÜK SICAKLARDA KULLNIMI**

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Bu çalışmada, HC-SCR sistemi için Ag/Cu esaslı katalizör emdirme yöntemiyle sentezlenmiştir. Bu sistemde indirgeyici olarak etil alkol ve saf su karışımı kullanılmış ve üretilen katalizörün NOx dönüşüm verimliliği üzerindeki etkisi incelenmiştir. Katalizöre ait SEM, XRD ve BET analizleri gerçekleştirilerek yapısal ve kimyasal özellikleri belirlenmiştir. SCR egzoz performans test sisteminde üretilen katalizör kullanılarak 170-260 $^{o}$C sıcaklık aralığında ve 2 farklı SV'de (20000 $h^{-1}$,40000 $h^{-1}$) deneyler yapılmıştır. Testler 2 silindirli V-tipi bir dizel motor kullanılarak sabit motor devrinde (3000 d/dk) ve 4 farklı motor yüklemesinde (1,2,3 ve 4 KW) gerçekleştirilmiştir. Bu testlerle, SCR katalizörünün NOx emisyonu üzerindeki etkisi tespit edilmiştir. NOx dönüşüm oranlarının 55% ile 68% arasında olduğu tespit edilmiştir. En yüksek NOx dönüşüm oranı 4 KW yük durumunda, %100 etil alkol püskürtülerek ve SV=20000$h^{-1}$ değerinde yaklaşık 68% olarak elde edilmiştir.

**Anahtar Kelimeleri:** NOx, SCR, İndirgeyici,Dizel motoru

## GENİŞLETİLMİŞ ÖZET

Çevreye ve İnsan sağlığına ciddi zaralar vermekte olan $NO_x$ emisyonları, iklimsel değişikliği ve küresel ısınmanın en temel kaynakları arasında gösterilmektedir. Tüm dünyada, $NO_x$ emisyonlarının minimize edilmesine yönelik birçok standartlar ve kurallar geliştirilmekte ve uygulanmaktadır. Çevreye salınan $NO_x$ emisyonları en çok Dizel motorlu taşıtlarının egzoz dumanında bulunmaktadır. Bu emisyonlar dizel motorları için ciddi bir problem olmuştu. Hükümetlerin uyguladığı emisyon standartlarının her geçen gün sıkılaşmasıyla birlikte NOx emisyonlarının çevre ve insan sağlığı üzerindeki olumsuz etkileri nedeniyle Otomotiv sektöründe taşıt üretimini durdurma veya dizel motor üzerindeki ar-ge çalışmalarını sonlandırma kararı verilmektedir. Fakat benzin motorlu taşıtlarla kıyaslandığında, Dizel motorlardaki yüksek dayanıklılığı, verimlilik, ve düşük yakıt tüketimi gibi özellikler motoru avantajlı hale getirmektedir. Özellikle ağır hizmet taşıtlarında dizel motorlardan vazgeçilmesi oldukça zor görülmektedir. Bunun için otomotiv üreticileri ve araştırmacıları $NO_x$ emisyonlarını azaltmak ve emisyon standart değerlerini sağlamaya yönelik bir arayış içerisine sokulmuşlardır.

Geçmişten bu yana $NO_x$ emisyonlarının azaltılmasına yönelik birçok sistem geliştirilmiş ve taşıtlara uygulanmıştır ancak bu sistemler emisyonun beklenen azalmalarını gerçekleştirememiştir. NOx emisyonlarının azaltması bir tek seçici katalitik indirgeyici (SCR) teknolojisiyle sağlanmıştır. SCR sistemi teknoloji 1970'li yıllara dayanmaktadır. Bu sistemde $NO_x$ emisyonları bir indirgeyici kullanılarak azot ($N_2$) ve suya dönüştürülmektedir. SCR sistemlerinde en yaygın olarak kullanılan indirgeyici türü amonyaktır. Amonyak %33 oranında üre çözeltisi ($(NH_2)_2CO$), ve %67 oranında saf suyundan ($H_2O$) oluşan ve AdBlue olarak adlandırılan sulu üre çözeltisinin egzoz gazına püskürtülmesiyle elde edilmektedir. SCR sistemlerinde en yaygın olarak kullanılan katalizör $V_2O_5$-$WO_3$/$TiO_2$ yapısına sahip, ve indirgeyici olarak Adblue solüsyonudur. $NO_x$ emisyonları özellikle 350-

450 $^{o}$C egzoz gazı sıcaklıklarında yüksek oranlarda minimize edilmektedir. Fakat 250 $^{o}$C'nin altındaki düşük egzoz gazı sıcaklıklarında dönüşüm verimliliği azaldığı ve katalizör yüzeylerinde amonyak birikmesi gözlemnlenmektedir.

İndirgeyici olarak HC'ların kullanımı SCR sisteminin düşük sıcaklıktaki dönüşüm verimliliği arttırmaktadır. Egzoz içeriğindeki yanmamış HC'ların ve dizel yakıtının indirgeyici olarak kullanımı sistemin maliyeti düşürmekte ve basitleştirmektedir. Metanol, etanol, ve propanol gibi içeriğinde oksijen barındıran bazı hydrokarbonlar $NO_x$ dönüşüm oranlarını iyileştirmekte oldukça etkilidir. Düşük egzoz gazlarında düşük performans sergileyen ve toksik etkiye sahip olan $V_2O_5$-$WO_3$/$TiO_2$ katalizörlerinden farklı olarak gümüş katkılı seramik yapılar (Ag-$Al_2O_3$) indirgeyici olarak HC'ların kullanıldığı SCR sistemlerinde (HC-SCR) iyi dönüşüm oranı sağlamaktadır. Gümüş haricinde paladyum (Pd), bakır (Cu), demir (Fe), platin (Pt), Kobalt (Co), rodyum (Rh) vb. birçok metal HC-SCR sistemlerinde katalizör olarak kullanılmıştır. Özellikle Pt esaslı katalizörler düşük egzoz gazı sıcaklıklarındaki NOx emisyonlarını azaltmakta yüksek performans sergilemişlerdir.

Bu çalışmada üretimi gerçekleştirilen Ag-Cu katalizöründe $NO_x$ emisyonlarının etanol kullanılarak seçici katalitik indirgenmesi üzerine odaklanılmıştır. Katalizöre ait analizler gerçekleştirilerek özel olarak tasarlanmış egzoz sistemi aracılığıyla farklı motor yükü, space velocity ve egzoz gazı sıcaklıklarında etanolun Ag-Cu katalizörü kullanılarak $NO_x$ dönüşüm verimliliği üzerindeki etkileri deneysel olarak araştırılmıştır. Katalizör üretimi, literatür bilgileri ışığında, Çukurova Üniversitesi Otomotiv Mühendisliğine ait laboratuarların altyapısı kullanılarak gerçekleştirilmiştir. Katalizör üretiminde, hazır olarak temin edilen 400 cpsi kare gözeneğe sahip kordiyerit ($2Al_2O_3$-$5SiO_2$-2MgO) ve monolith ana taşıyıcı yapı kullanıldı.

HC-SCR sistemi için Ag/Cu esaslı katalizör emdirme yöntemiyle sentezlenmiştir. Ilk önce Kordiyerit tartırıldı sonra fırında 110$^{o}$C sıcaklıkta 1 saat boyunca ısıtıldı. Kordiyerit yapının kaplanması amacıyla gümüş esaslı solüsyon

hazırlandı. Solüsyon hazırlamak için 500 ml distile suyun içine 10,1g g gümüş nitratın ($AgNO_3$) yanı sıra 5,2g bakır (II) nitrat trihidrat ($Cu(NO_3)_2.3H_2O$) eklenerek ultrasonik karıştırıcıda yaklaşık 20 dakika boyunca karıştırıldı. Elde edilen solüsyona kordiyerit malzeme daldırıldı. Daldırma işleminden sonra kordiyerit malzeme fırında 110$^oC$ sıcaklıkta 1 saat boyunca kurutuldu. Daha sonra bu malzemeler 600$^oC$ sıcaklıkta 5 saat kalsine edildi. Böylece katalist yapıların üretimi gerçekleştirildi.

Sonuç olarak, Katalizöre ait SEM, XRD ve BET analizleri gerçekleştirilerek yapısal ve kimyasal özellikleri belirlenmiştir. SCR egzoz performans test sisteminde üretilen katalizör kullanılarak 170-260 $^oC$ sıcaklık aralığında ve 2 farklı SV'de (20000 $h^{-1}$,40000 $h^{-1}$) deneyler yapılmıştır. Testler 2 silindirli V-tipi bir dizel motor kullanılarak sabit motor devrinde (3000 d/dk) ve 4 farklı motor yüklemesinde (1,2,3 ve 4 KW) gerçekleştirilmiştir. Bu testlerle, SCR katalizörünün NOx emisyonu üzerindeki etkisi tespit edilmiştir. NOx dönüşüm oranlarının 55% ile 68% arasında olduğu tespit edilmiştir. En yüksek NOx dönüşüm oranı 4 KW yük durumunda, %100 etil alkol püskürtülerek ve SV=20000$h^{-1}$ değerinde yaklaşık 68% olarak elde edilmiştir.

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**LIST OF ABREVIATIONS AND NOMENCLATURE**

| | |
|---|---|
| C | : Celsius |
| Ag | : Silver |
| F | : Fahrenhiet |
| Cu | : Copper |
| KW | : Kilowatt |
| XRD | : X-ray Diffraction |
| XRF | : X-ray Fluorescene |
| BET | : Brauner– Emmett – Teller |
| DOC | : Diesel oxidation catalyst |
| SCR | : selective catalytic reduction |
| NOx | : Oxides of Nitrogen |
| SOx | : Sulfur Oxides |
| PM | : Particulate matter |
| CO | : Carbon monoxide |
| VOC | : Volatile organic compounds |
| EGR | : Exhaust gas recirculation |
| DPF | : Diesel particulate filter |
| TWC | : Three-way catalytic converter |
| LNT | : NOx-storage catalyst |
| $AgNO_3$ | : Silver nitrate |
| $CuH_2N_2O_7$ | : Copper(II) Nitrate Trihydrate |
| SV | : Space Velocity |
| EURO | : European |

# 1. INTRODUCTION

Internal combustion engines have played an important role in our life since its invention. These engines turn chemical energy to electrical or mechanical energy we can use and thus it decreases human labor and facilitates our lives. Currently, Combustion of fossil fuel from power plants, transportation, and industrial factories causes air pollution which has a harmful effect on the environment and human health (Gill, 2012).

One of the most prevalent vehicles in the automotive sector today are heavy duty vehicles, they're used for shipping goods and resources to satisfy humans and industry's needs. Diesel engine is the main power of these vehicles because of its fuel efficiency. However, due in incomplete combustion, it emits very harmful gases that cause intense hazards to the environment (King, 2007). Diesel engines emissions contain greenhouse gases; a greenhouse gas is a gas that traps heat (long wave radiation heat) and by doing so causes earth to warm. The most known greenhouse gases are methane ($CH_4$) that exists in animal agriculture, Carbon dioxide ($CO_2$) that is a main cause of global warming, and other fluorinated gases (CFC). In diesel engines emissions, the greenhouse gases are Carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) that derives from Nitrogen oxides (NOx) (Schmitt, 2010). Global warming leads to climate changes that take the form of unstable water systems, heat waves, weather storms, floods, and hurricanes; also, it has a negative impact on food and water supply, and can lead to change in vector borne disease (Pereira, 2009). The transportation sector produces the highest $NO_x$ pollution (40.5%), according to the European Environment Agency (EFA). The need to remove $NO_x$ gases have been emphasized especially in Diesel engines that are spreading in the market more rapidly than gasoline engines, and that have more $NO_x$ emissions because of its different operating conditions. $NO_x$ comprises nitric oxide (NO) and nitrogen dioxide ($NO_2$) that is produced in combustion. NO and $NO_2$ are available in nature and are produced through thunderstorms. But, when the

concentration of $NO_x$ gets significantly higher, it produces negative effects on the environment and health. $NO_x$ causes the formation of nitric acid that forms acid rains, and causes lakes and the oceans to acidify. This acidification has a negative impact on building materials, and in addition to the formation of ground level ozone that is dangerous to human's health, it destroys the ozone in the stratosphere which causes harm to humans, animals, and plants. It is estimated that over 30 million tonnes of $NO_x$ are emitted into the atmosphere per year. The main source of $NO_x$ emissions in the world is motor vehicles (Tamaldin, 2010; Nobuwaka, 2006; Ivaturik, 2007).

Recently, Nitrous oxide ($N_2O$) which derives from nitrogen oxides ($NO_x$), has been extensively researched and discussed due to its high amounts in the atmosphere, and because it is a greenhouse gas, it causes ruptures in the ozone layer. $N_2O$ gas has a lifetime of approximately 150 years in the atmosphere, $N_2O$ has 310 times the global warming potential (GWP) of $CO_2$, and 14.8 the potential of $CH_4$, so it is has a big contribution to global warming and decreasing its concentrations in the atmosphere would help decrease global warming (Ivaturik, 2007). For the reasons above, Scientists have been doing more research and experiments to improve the $NO_x$ reduction rate using the most efficient DeNOx technologies in the automotive sector. This mission is getting more difficult due to the increasingly tightened emissions standards.

# 2. DIESEL ENGINES AND EMISSIONS

## 2.1 Diesel engines

The diesel engine was created in the last century by Rudolf Diesel (1893). However, it was Robert Bosch who made the engine more efficient by developing a convenient diesel fuel injection pump (Radtke, 1996). Diesel engines are known as internal combustion (IC) engines that operate by harnessing the heat that is produced from compressing an air charge to combust the air-fuel mixture (A/F) through a process called compression ignition (CI). The combustion process in diesel engines occurs in four separate steps: air enters the combustion chamber; then gets compressed by a piston to a high pressure that results in a tight space of hot compressed air to which fuel droplets gets injected directly or indirectly by a fuel injector causing combustion to happen evenly in the engine. After the combustion occurs, the fuel droplets vaporize and the pressure increases in the combustion chamber, which causes a fast expansion that result in the piston supplying power downward to the crankshaft (Sitshebo, 2010). The typical heavy-duty and light-duty diesel engine's combustion process is shown in Figure 1.1 below:

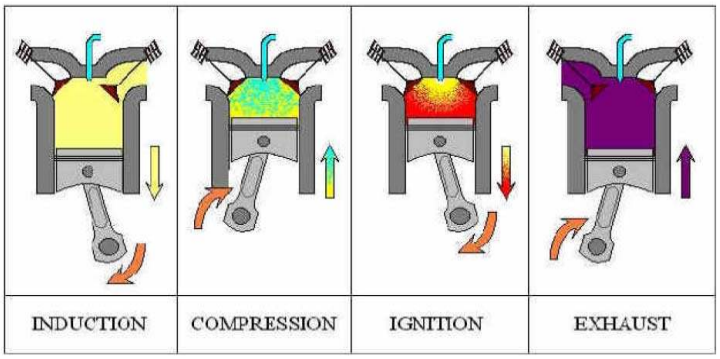


Figure 2.1. The four cycles of a combustion of a di0esel engine (Crystle, 2012)

Diesel engines have been occupying a very important role in the automotive industry compared to Gasoline engines due to several reasons: they have important advantages over their counterpart gasoline spark ignition (SI) engines, such as, improved fuel economy and high efficiency because of throttling absence, the overall lean mixture, the considerably higher compression ratios, and long-term engine durability, as the engine is normally designed to withstand compression ratios that are high (Sitshebo, 2010; Sitshebo, 2009). In addition, Diesel engines are more widespread today because they have lower $CO_2$ footprints than gasoline engines, which mean they are better to the environment than gasoline engines as far as global warming is concerned. For example, in Europe 50% of vehicles are now diesel engines vehicles (Radtke, 1996). Although, exhaust after-treatment systems are still essential to decrease the amount of harmful gases like nitrogen oxides ($NO_x$) produced in the exhaust of the engine mainly because of diesel lean operations. The fuel delivery pressure, the quantity of the fuel delivered, and the fuel delivery system are important components that affect the diesel engine's efficiency and thus increase its exhaust emissions.

These days, diesel engines work with a totally electronically controlled common rail direct injection system that is able of great injection pressure (>1800 bar), together with the recent technology that utilizes piezoelectric fuel injectors for higher spray precision in the combustion chamber, which in turn, can employ multiple injections into a single cylinder in any one engine cycle. The advantages over other models are better fuel economy, minimized emissions, and lower engine noise (Sitshebo, 2010; Joshua, 2010).

### 2.2. Emissions from Diesel engines

Our atmosphere normally contains air that is a combination of gases that are surrounding the earth. Pure air is composed of 78% nitrogen and 21% oxygen, plus a residue of other matter and gas that can be natural or man-made. The air comprises also chemical and biological stuff that are mainly pollutants, like, for

example, fine particulate matter PM (they have a size of 2.5 microns in diameter, sulphur dioxide ($SO_2$), ground level ozone $O_3$, nitrogen oxides ($NO_x$), volatile organic compounds (VOCs), nitrates($NO_3$), and Sulphate ($SO_4$). Diesel engines emissions have a big share in these pollutants (Santillan, 2011).

Next we look at how these emissions form and their negative effect on health and the environment. Because of incomplete combustion, large quantities of pollutants are released to the environment from diesel engines:

### 2.2.1. Volatile organic compounds (VOC)

Volatile organic compounds (VOCs) are characterized by having low water solubility and high vapor pressure, they're also known as HC fuel components and their formation depends to a large degree on the mixing degree with the combustion temperature in the combustion chamber. Various VOC forms can be produced with different fuel types like biodiesel or diesel by relying on pyrolysis with high temperature, medium thermal cracking, and mild oxidation processes that occur in the combustion chamber, and depolymerisation. Despite its abundance in nature and industrial community, they can be toxic and harmful. Its negative impact on health depends upon the duration of exposure, the intensity of exposure, and the type of compound exposed to. The harmful effects of VOC can include nose, eye, and throat irritation; also it causes loss of coordination, liver damage, and harms the central nervous system, and even cause cancer in animals and humans (Andreas, 2016; Radtke, 1996; Nigel, 2007).

### 2.2.2. Sulfur oxides ($SO_x$):

They are mostly produced as a result of oxidation of fuel-bound sulfur; $SO_2$ dissolves in water to form sulfuric acid that harms plants and animals by forming acid rain. $SO_2$ forms regional haze and fine particulate that cause visibility impairment; $SO_2$ is a respiratory irritant and it might aggravate existing respiratory

illness; long periods exposure leads to chronic bronchitis (Radtke, 1996; Fredrik, 2016; Andreas, 2016).

### 2.2.3. Particulate matter(PM):

PM can be defined as any exhaust gas material that could a sampling filter medium trap at 52 °C (125 °F) or even less; Examples of Particulate matter are soot (carbonaceous matter), soluble organic fraction (like high boiling hydrocarbons and their derivatives), dust, inorganic materials present in fuel additives, and sulphate particles. PM is usually solid or liquid particles (includes ash and soot...) that range in size up to 50 micrometers (μm) in diameter. In a diesel engine's exhaust system the particle size is classified into three groups: the nuclei mode particles that have a diameter from 5-50nm and they represent the exhaust gas dilutes and cools; the accumulation mode particles that has a range between 30 and 500nm, and they comprise adsorbed material and carbonaceous agglomerates; coarse mode particles that are usually larger than 1 μm and contains restrained mode particles that were deposited on exhaust system surfaces and cylinders (Fredrik, 2016; Andreas,2016; Nigel,2007; Resitoglu, 2015 ). The health effects of PM emissions can be manifested as breathing and respiratory problems, aggravation of an existing cardiovascular illness, harm caused to lung tissue and decline in the body's defense mechanisms. Prolonged exposure to particulate matter aggravates bronchitis, asthma, and diminishes lung function (Radtke, 1996).

### 2.2.4. Carbon monoxide (CO):

CO is an odorless, gas that is produced due to incomplete oxidation (burning). Its formation increases due to the lack of oxidants (e.g. $O_2$ in air), residence time throughout the combustion process and temperature. CO formation process in hydrocarbon combustion is intermediary and can be showed in the following equation with R referring to the HC radical (Gill, 2012; Radtke, 1996).

$$RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO \quad (2.1)$$

The highest quantities of CO are usually the product of fuel-rich mixtures because of oxidant's absence, however, due to the lean cycle diesel engines operate on, a large quantity of air is available to oxidize CO to $CO_2$ as shown in the equation (1). The reaction of hydrocarbons continue in the exhaust at temperature above 600°C in the presence of oxygen, this is why tailpipe hydrocarbon emissions may be much lower than hydrocarbons that leave the cylinder. In general, CO emissions are generally low in a diesel engine (Herdzik, 2011):

$$CO + OH \rightarrow CO_2 \quad (2.2)$$

In case of inhalation, carbon monoxide attaches to the oxygen-carrying site on the blood's hemoglobin, and thus hinders the blood carrying capacity of oxygen. The degree of saturation of the hemoglobin with carbon monoxide determines the symptoms of exposure as it aggravates the risk of death as saturation increases. The intensity of hemoglobin saturation mostly depends on the oxidation of CO and the time of exposure. At high amounts it is very toxic, causes nausea, dizziness, and headaches and hinders the ability to think (Resitoglu, 2015; Radtke, 1996; Herdzik, 2011).

### 2.2.5. Oxides of nitrogen ($NO_x$):

When fuel is burnt at high temperatures (above 1,600°C) and high pressures, nitrogen reacts with oxygen in the cylinder and produce $NO_x$ gases; what influences the formation of $NO_x$ could also be the residence time, amounts of reacting species, and flame conditions. The Zeldovich mechanism below shows us the equations by which $NO_x$ is formed (Gill, 2012; Radtke, 1996; Sedlmair, 2002; Pereira, 2009).

$$O + N2 \leftrightarrow NO + N \quad (2.3)$$

$$N \mid O2 \leftrightarrow NO \mid O \quad (2.4)$$

$$N + OH \leftrightarrow NO + H \quad (2.5)$$

At typical flame temperatures, $NO_2$/NO ratios must be small to maintain a chemical equilibrium, but this ratio is approximately 30% of the total oxides, and the cause of this is $NO_2$ emissions; $NO_2$ formation can be explained in the equation (6) below:

$$NO \mid HO_2 \rightarrow NO_2 \mid OH \quad (2.6)$$

The following equation represents what happens when decay occurs:

$$NO_2 + O \rightarrow NO + O_2 \quad (2.7)$$

Equation (7) above displays the conversion of $NO_2$ to NO that happens when produced $NO_2$ is not extinguished while being mixed with cool fluid in the combustion chamber. High $NO_2$ formation takes place especially for engines that operate at low load, thus resulting in lower combustion temperatures, and hindering $NO_2$ decomposition (Gill, 2012; Nigel, 2007; Resitoglu, 2016). $NO_x$ emissions are produced from the beginning of the combustion process, when the piston is still close to the top of its stroke, a time when the flame temperature is at its peak, when the combustion temperature gets increased and the amount of $NO_x$ increases three times as much for every 100°C increase.

The transportation sector is the most significant contributor to $NO_x$ emissions in the world; it contributes between 40-70% of the total $NO_x$ emissions. Compared to gasoline engines, diesel engines powered vehicles are the highest contributors to $NO_x$ emissions (about 85%), most of these emissions are in the form of NO. NOx gases are present in the atmosphere as nitrogen oxide (NO), nitrogen dioxide ($NO_2$) and nitrous oxide ($N_2O$); NO represents approximately 80–90% of $NO_x$. $NO_x$ gases can react with unburned hydrocarbon (HC) or VOC when sunlight is available in lower atmospheres leading to ground level ozone which causes human respiratory problems, irritates the eyes and damages plants; $NO_x$ gases react with water to form $HNO_3$ that causes acid rains that can make building materials and paints decay rapidly; $NO_x$ undergo chemical reactions that bring about photochemical smog; Airborne nitrate and nitrogen dioxide can cause pollutant haze that impairs visibility. The negative effects intensity depends on the level and duration of exposure. For example, NO can react with hemoglobin in blood which produces fatal meta-hemoglobin at high levels; $NO_2$ when breathed can damage lungs severely (Sedlmair, 2002; Resitoglu, 2016; Ezike, 2011).

**2.2.6. Smoke:**

Very rich A/F ratios or fuel evaporated in part during cold start conditions can lead to poor combustion that eventually leads to the formation of smoke. Smoke comes in two forms: black smoke and white smoke; white smoke is comprised of lubricating oil particles and fuel that is partially burned, it is also known as liquid smoke; black smoke, on the other hand, comprises solid carbon particles that resulted from complete combustion of HC fuel. The smoke can be classified into two forms, namely, white smoke and black smoke. White smoke consists of fuel and lubricating oil particles in an unburned or partially burned state, more commonly referred to as liquid smoke or fog. Whereas, black smoke consists of solid carbon particles from complete combustion of the HC fuel, usually known as hot solid smoke. Smoke health effects are similar to those of PMs

because Smoke is made of very fine particles that are easy to breathe (Ezike, 2011; Solt, 2011).

### 2.2.7. Carbon dioxide ($CO_2$):

Carbon dioxide is a greenhouse gas that causes Global warming in the long-term but considered benign to humans and not among the Toxic gases that affect human's health in the short term (Solt, 2011; Lintunen, 2001).

# 3. EMISSIONS REGULATION AND MINIMIZATION

## 3.1. Emissions standards regulations:

The most important legislations nowadays are European legislation or EURO. EURO I emission standards started off in the 1990s and over the years the regulations got more stringent until finally the EURO 6 was implemented in 2014 and still to this day (Constantinou,2012;Gill,2012).

Table 3.1. Emissions reductions According to the European Union regulations (Anonymous 1)

| | CO(g/KWh) | HC(g/KWh) | NOx(g/KWh) | PM(g/KWh) |
|---|---|---|---|---|
| Euro I | 4.5 | 1.1 | 8.0 | **0.61** |
| EuroII | 4 | 1.1 | 7.0 | **0.15** |
| EuroIII | 2.1 | 0.66 | 5.0 | **0.13** |
| EuroIV | 1.5 | 0.46 | 3.5 | **0.02** |
| EuroV | 1.5 | 0.46 | 2.0 | **0.02** |
| EuroVI | 1.5 | 0.13 | 4.0 | **0.01** |

Table 3.2 shows the emissions abatement development for M1 and M2 (passenger cars), N1 and N2 (commercial cars) vehicles throughout the years 1990 to 2014. The unit of the emissions in the table is mass per energy (g/kWh). We can notice how much the amount of pollutants are being decreased like for particulate matter PM; at EURO I, it was 0.61 g/kwh compared 0.01 at EURO 6; a significant decrease.

To design a new diesel engine that meet the ever stringent regulations, a lot of modifications have been applied like improvement of fuel used, using technologically advanced electronic fuel injection systems .etc. All of that can achieve some abatement of emissions but not enough to meet the emissions regulations; Currently PM and $NO_x$ emissions from diesel engines are close to the

limits imposed by EURO 6 which means that we have to use more advanced after treatment technologies to decrease $NO_x$ emissions especially due to its large amount in the exhaust system (Gill, 2012; Su, 2009).

### 3.2. Emissions control systems:

To comply with European emissions standards, many emissions control systems have been developed by engineers to deliver efficient results in reducing harmful emissions to the minimum. These emissions control systems were: exhaust gas recirculation (EGR), lean NOx trap (LNT), and SCR (Su, 2009).

#### 3.2.1. Exhaust gas recirculation (EGR):

EGR has been a main method to control the formation of $NO_x$, by manipulating the concentration of Oxygen in the cylinder and thermodynamic properties while at the same time maintaining lower degradations in efficiency and power (Reşitoglu, 2015). In addition to the $O_2$ reduction, $CO_2$ addition, $N_2$, and water vapor ($H_2O$) use, EGR decreases flame temperature whilst bringing up the total heat capacity of the cylinder charge. So EGR diminishes the rise of temperature of the same heat release occurring in the combustion chamber (Sitshebo, 2010).

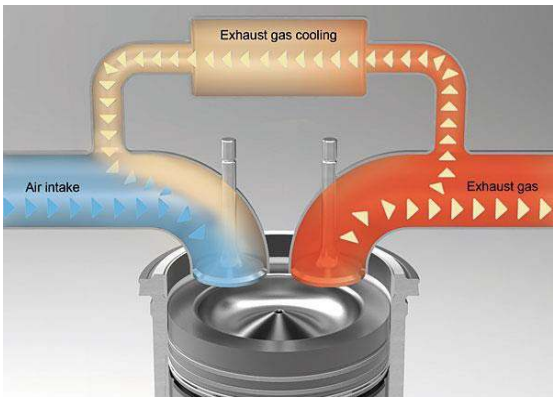


Figure 3.1. Exhaust gas recirculation in EGR schematic (Anonymous 2).

In order to reduce $NO_x$ emissions, exhaust gas gets recirculated back into the combustion chamber and mixed with fresh air at intake. EGR, however, cannot by itself achieve the desired reduction in $NO_x$, plus, it generates HC and CO emissions due to reduction in combustion temperature (Gill, 2012). Even if EGR is effective in reducing $NO_x$ emissions, it exacerbates the PM/NOx trade-off, under higher loads in particular where diesel combustion is able to produce more smoke due to the fuel rich places having difficulties finding oxygen at the last combustion stages. Also, soot is formed in the diffusion flame after coagulation steps and serial growth. Soot and $NO_x$ forms in hydrocarbon combustion in accordance with the equivalence ratio (fuel/air ratio), and temperature. EGR leads to an increase in PM, so to comply with strict emissions regulations, more effective control systems must be used (Gill,2012; Reşitoglu,2015 ).

### 3.2.2. Diesel oxidation catalyst (DOC):

A diesel oxidation catalyst (DOC) is a device that makes use of a chemical reaction to convert diesel engine's exhausts to harmless gases (Gill, 2012). The chief role of DOCs is to oxidize CO and HC emissions. Moreover, DOCs play an important role in decreasing the mass of diesel particulate emissions by oxidizing some of the hydrocarbons that are adsorbed onto the carbon particles. DOCs are also used with SCR catalysts to oxidize NO into $NO_2$ and increase the $NO_2$: NOx ratio (Reşitoglu, 2015; King, 2007). Three main reactions of DOCs are:

$$CO + {}^{1}/_{2}\,O_2 \rightarrow CO_2 \tag{2.8}$$

$$C_3H_6 + {}^{9}/_{2}\,O_2 \rightarrow 3CO_2 + 3H_2 + 3H_2O \tag{2.9}$$

$$NO + {}^{1}/_{2}\,O_2 \rightarrow NO_2 \tag{2.10}$$

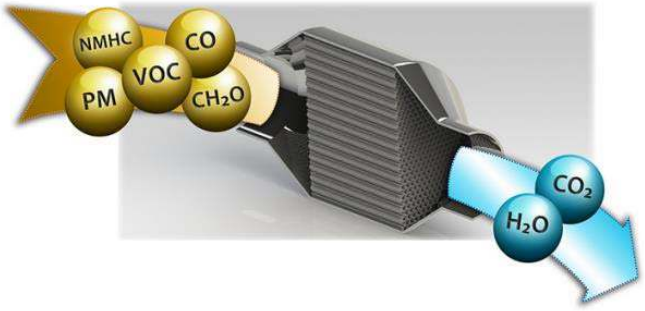


Figure 3.2. Diesel catalyst (Anonymous 3)

Equation (10) shows additional oxidation of NO to $NO_2$. $NO_2$ has gained interest because it can facilitate passive DPF regenerations and improve the performance of some SCR catalysts. Adsorption of $O_2$ is conducted by the active catalytic sites that are the key to reaction process. Generally, oxidation of the catalyst includes Oxygen that binds to the catalytic sites, HC and CO reactants that diffuse and react with oxygen on the surface and thus forms $CO_2$ and $H_2O$ as reaction products (figure 3.2). DOC can to only a small extent, reduces $NO_x$, but this reduction occurs just within certain temperature window. Few suggestions are presented to use $NO_2$ that comes out of the engine to oxidize the accumulated soot in the catalyst. Platinum (Pt) and base metal palladium were considered best catalyst choices. (Reşitoglu, 2015).

### 3.2.3. Diesel particulate filters (DPF):

DPFs or wall flow filters are applied to remove PM/soot emissions by physical filtration and usually made of cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$) or silicon carbide (SiC) honeycomb structure monolith with the channels blocked at alternate ends (Sawatmongkhon,2011).

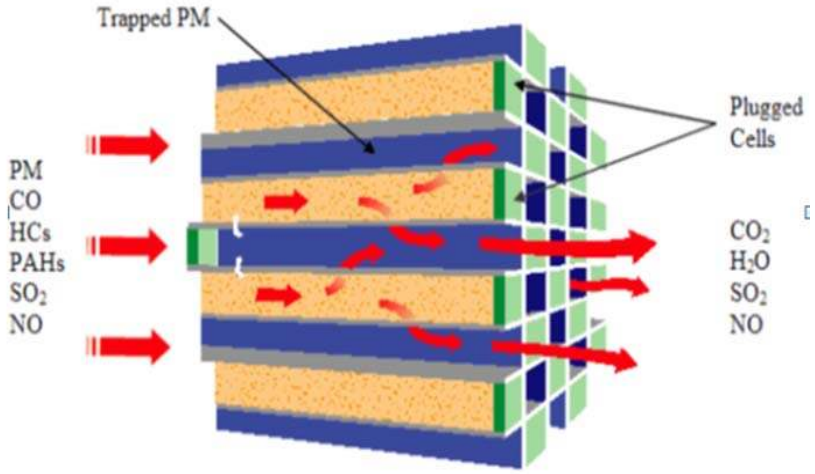


Figure 3.3. Diesel particulate filter (Hyerim et al.,2015)

The exhaust gas permeates into the walls through ordered square channel, thereby trapping the soot particles inside the porous wall, and over the inlet channel surfaces. As soot (PM) accumulates in the filter, it builds up back pressure that has many harmful effects such as increased fuel consumption, engine failure and stress in filter, which calls for a process called regeneration. Hence, two types of regenerations are used: active and passive regeneration: In active regeneration (active filters), PM is oxidized periodically by outside heat, such as from an electric heater or flame-based burner (Sitshebo, 2010). Active regeneration is not preferable because the high production cost. In passive regeneration, the source of heat is the exhaust gas stream itself. In this type of filter system, the filter regenerates incessantly as long as the engine is on. Passive filters usually include a catalyst that lowers the soot oxidation temperature so that it can be reached by exhaust gases during the operation of the vehicle Regeneration remains a problem for DPFs though (Sitshebo, 2010; Reşitoglu, 2015; Hyerim et al., 2015).

### 3.2.4. Three-way catalytic converter (TWC):

TWC was one of the most successful and pervasive way to deal with $NO_x$ emissions catalytically and convert them to benign $N_2$ by unburned hydrocarbons (HCs), CO and $H_2$ on supported precious metals including Pt, Rh and Pd. And, at the same time oxidize HCs and CO to $CO_2$ and $H_2O$. In diesel engines, however, TWC is not that effective because instead of reducing $NO_x$ to $N_2$, unburned HCs oxidize with the abundant amount of $O_2$ available (Hyerim et al., 2015).

### 3.2.5. NOx Storage Catalyst (LNT):

This technology involves $NO_x$ adsorption during lean conditions and $NO_x$ reduction (also referred to as the regeneration) during rich periods. The $NO_x$ storage catalyst consists of three key components: i) an oxidation catalyst (e.g. Pt), ii) a $NO_x$ storage medium (e.g. barium oxide (BaO)) and iii) a reduction catalyst (e.g. Rh) (Reşitoglu, 2015; Hyerim et al., 2015).

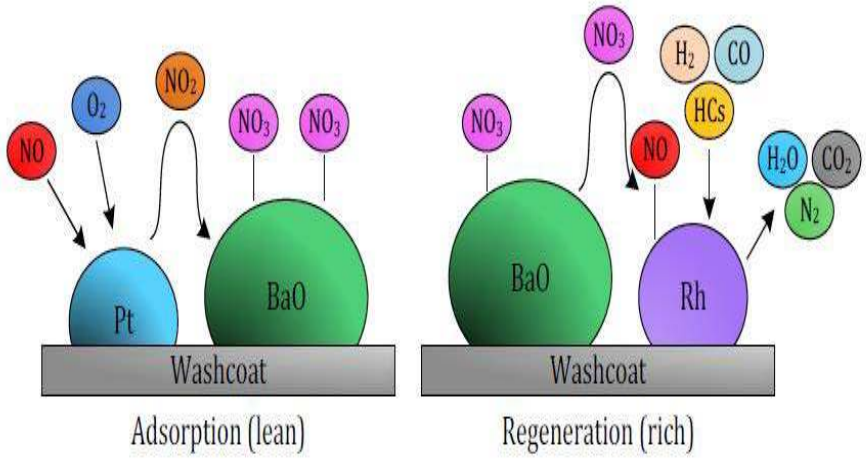


Figure 3.4. $NO_x$ adsorption and regeneration schematic (Hyerim et al., 2015)

The adsorption and regeneration process of NOx consists of:

-In the first stage, NO is oxidized to $NO_2$ by reacting with the oxygen on the catalyst site Pt as illustrated in the following equation:

$$NO+{}^{1}/_{2}O_2 \rightarrow NO_2 \quad (2.11)$$

- The second stage involves the migration of $NO_2$ particles from Pt sites to the NOx storage sites (BaO):

$$BaO+2NO_2+{}^{1}/_{2}O_2 \rightarrow (NO_3)_2 \quad (2.12)$$

- Reduction phase: the engine is switched to rich mode; HCs, CO and $H_2$ take the place of Oxygen (Sawatmongkhon, 2011).

- Nitrate species are released and then gets decomposed to form NO that gets removed on the Rh sites. The equation below illustrates the process:

$$(NO_3)_2 \rightarrow BaO+2NO+{}^{11}/_{2}O_2 \quad (2.13)$$

- NO is reduced by HCs, CO and hydrogen to produce $N_2$ on the reduction catalyst, in a process that happens on the TWC:

$$NO+CO \rightarrow 1/2N_2+CO_2 \quad (2.14)$$

Still, there are a number of other problems with the LNT method: Sulphur compounds that are present in the exhaust react with a $NO_x$ storage medium to form sulphates which accumulate gradually on the active catalyst surface during lean conditions. This makes the $NO_x$ storage medium saturated with sulphates and lost active sites for $NO_x$ adsorption (Sawatmongkhon, 2011).

### 3.2.6. Selective Catalytic Reduction (SCR):

SCR control system is the system that attracted the most attention in the last decades; it is one of the most widespread technologies in the treatment of $NO_x$ emissions; $NO_x$ exhausts are usually composed of 95% NO and 5% $NO_2$ (More, 2016). Selective Catalytic Reduction (SCR) is an emissions control system that reacts catalytically with a reductant agent on a catalyst. Catalyst materials examples are ion-exchanged zeolites, Cu, Pt and Ag. Catalysts supports examples include $AL_2O_3$, $SiO_2$, $ZrO_2$ and $TiO_2$. Pollutants get converted into nitrogen ($NO_2$), water ($H_2O$) and tiny amounts of $CO_2$ (Reşitoglu, 2015). SCR technology was first used in power plants in Japan (1970) and stationary industrial sources; at first SCR used ammonia as a reductant ($NH_3$-SCR). With injection of $NH_3$ to give $N_2$ and $H_2O$ as products, the equation that governs the reaction of $NO_x$ (equation (15) coming of the engine gets catalyzed by a metal oxides mixture, like $TiO_2$, $WO_3$, and $V_2O_5$ (Devadas, 2006).

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (2.15)$$

When SCR started getting applied in the automotive industry on heavy-duty vehicles and recently on light-duty vehicles, ammonia presented partial solutions and included serious drawbacks: it is hazardous and toxic, plus, high vapor pressure makes it a challenge to store safely. Ammonia later, have been replaced by Urea solution. Urea-SCR has great deNOx efficiency and has been extensively used for heavy and light-duty vehicles alike. In Urea-SCR, the toxic ammonia is converted chemically to an odorless, non-toxic, solid, highly soluble in water urea, but still there is the problem of installing of urea tanks on board, problems of ammonia slip and urea freezing ((N$H_2$) 2CO) (Sawatmongkhon, 2011; Raya et al, 2015).

The Urea-SCR $NO_x$ reduction involves the following steps:

-Urea solution gets sprayed on exhaust gas and then an endothermic decomposition occurs melting urea solid particles and producing ammonia and isyocanic acid in a reaction known as thermolysis:

$$(NH_2)2CO \rightarrow NH_3 + HNCO \quad (16)$$

-Isyocanic acid reacts with exhaust water in a reaction known as hydrolysis:

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (17)$$

-Further chemical reactions occur to selectively reduce $NO_x$ by conversion to nitrogen and water:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (18)$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \quad (19)$$

$$4NH_3 + 3NO_2 \rightarrow 3\,1/2\,N_2 + 6H_2O \quad (20)$$

The reactions above are called respectively the standard SCR and fast SCR reactions (Reşitoglu, 2015). NO accounts for approximately 90% of $NO_x$ emissions, which makes faster rate of conversion in the reactions above. For that reason, an $NO_2$ to NO fraction of 1:1 can be sought after by installing an oxidation catalyst before the SCR catalyst. Any excess more than the fraction of 1 and a much slower reaction will occur: As we've seen, Urea-SCR can be a good solution to $NO_x$ emissions, but few problems make it a non optimal solution: high cost of

installation, ammonia slip and convenient infrastructure for urea supply, and urea freezing. So, other reductant should be considered (Hyerim, 2015).

#### 3.2.6.1. Hydrocarbon SCR (HC-SCR):

To overcome the drawbacks of previous $DeNO_x$ systems, Selective catalytic reduction of $NO_x$ using Hydrocarbons (HC-SCR) has been getting a lot attention in recent times. One of its advantages is the availability of the reductants in the exhaust without the need for an additional installment of reductant (Joshua, 2010; Fredrik, 2016). HC-SCR is one of the most promising technologies in removing $NO_x$ emissions from vehicles operating under lean-burn conditions to help overcome the problems with previous deNOx technologies and its drawbacks. Any hydrocarbons such as Diesel-type fuels (e.g. diesel, synthetic diesel and biodiesel) can be used as a reductant, so, it is not necessary to equip the system with an extra tank for the reductant. Because of the abundance of hydrocarbons in diesel fuels, the investigation of different hydrocarbons on the SCR activities have been researched and cited in lots of scientific papers. Light hydrocarbons (i.e. propene and propane) have been broadly studied to discover the mechanistic fundamentals of HC-SCR (Guangyan et al., 2017; Andreas, 2016; Ahmad et al., 2017).

#### 3.2.6.2. Reductants for HC-SCR:

As can be seen in Table 3.3, different types of hydrocarbons in SCR have been studied as reductants such as lower hydrocarbons (C1-C4), higher hydrocarbons(>C6), diesel fuel and alcohols. The efficiency of catalytic reduction of $NO_x$ to $N_2$ by hydrocarbons was in the order alkanes < alkenes< oxygenated (Hyuk, 2004). Oxygenated hydrocarbons like ethanol is one of the most effective reductants, it could be made from renewable energy sources and be mixed with other diesel fuel, like a mixture of ethanol and of n-dodecane and m-xylene. Ethanol, acetone, and propanol have high conversion efficiencies of NOx (above

80%) at 250-400°C (Ahmad et al., 2017). With alumina-supported silver catalyst, NO reduction rate was ordered as 2-propanol > acetone > ethanol > 1-propanol >methanol at 350 °C. Isobutanol (iBuOH) has also attracted some attention as a reductant and proved to have some advantages over ethanol. It can works as an effective $NO_x$ reductant with $Ag/Al_2O_3$ as a catalyst, with a conversion efficiency of over 90% in temperatures between 300°C and 400°C. Long chain alkanes, like diesel or synthetic diesel fuel showed good improvement at low temperatures (200°C); short chain alkanes (e.g.ethane, propane, and isobutene) and alkenes (e.g. ethene and propene) and diesel type fuel (long chain hydrocarbon) were also used as reductants with $Ag\text{-}Al_2O_3$. A large portion of the exhaust HCs are short chain species products of fuel diesel combustion (Andreas, 2016; Simbarashe, 2010 ; Pavan,2016 ; Claes,2007).

Table 3.2. Hydrocarbons Reductants for HC-SCR and their formulas (Guangyan et al., 2017).

| Some of the Hydrocarbons studied as reductants | Formula |
|---|---|
| **Methane** | $CH_4$ |
| **Ethane** | $C_2H_6$ |
| **Propane** | $C_3H_8$ |
| **n-Butane** | $C_4H_{10}$ |
| **n-Pentane** | $C_5H_{12}$ |
| **n-Hexane** | $C_6H_{14}$ |
| **n-heptane** | $C_7H_{16}$ |
| **Cyclohexane** | $C_6H_{12}$ |
| **n-Octane** | $C_8H_{18}$ |
| **Propene** | $C_3H_6$ |
| **Methylcyclohexane** | $C_7H_{14}$ |
| **Benzene** | $C_6H_6$ |
| **Toluene** | $C_7H_8$ |
| **Cumene** | $C_9H_{12}$ |

**3.2.6.3. Reductant choice:**

The chosen reductant has a great effect on the outcome of the $NO_x$ conversion process. Long hydrocarbons with a chain length of a 6-12 carbon atoms have showed good activity for lower temperatures, compared to shorter chain hydrocarbons; partially oxidized hydrocarbons had also a similar result, but still, unoxygenated hydrocarbons weren't effective below 300 °C (Jasmeet, 2005).

**3.2.6.4. Catalysts for HC-SCR:**

Since it was first adopted in 1990, a big number of catalysts were studied: ion-exchanged zeolite catalysts (e.g. Cu-ZSM-5) showed high $NO_x$ reduction by hydrocarbons and wide window temperature, and high tolerance to catalyst deactivation caused by sulphur poisoning and coke deposition. However they were unstable in hydrothermal conditions. Copper-aluminum oxide catalysts (Cu-$Al_2O_3$) have been studied also; The Cu-$Al_2O_3$ with 16 wt.% Cu content exhibited higher activity than Cu-ZSM-5 at low temperature. Furthermore, the Cu-$Al_2O_3$ showed higher hydrothermal stability than Cu-ZSM-5. Ag/$Al_2O_3$ showed high activity for $NO_x$ reduction but Cu-$Al_2O_3$ showed high activity for unfavorable $C_3H_6$ oxidation. After zeolites, Platinum-based catalysts showed an excellent metal group for $NO_x$ reduction at low temperatures (200-250°C) and stability in water and sulphur; Pt-beta catalysts are effective with propene under excess of oxygen with a $N_2$ selectivity of 35% and no catalyst deactivation; Pt/ZSM5 prepared by liquid ion-exchange, and Fe/ZSM5 prepared by sublimation of $FeCL_3$, are among the most efficient catalysts for HC-SCR using isobutene as a reductant. Pt-Rh alloys have also displayed promising performance as catalysts for HC-SCR. However, one of their disadvantages is the formation of nitrous oxide, the extremely active greenhouse gas. Hybrid catalysts, the combination of different catalysts (e.g. the reduction of $NO_x$ by $CH_4$ on Pd-sulfated $CeZrO_2$) were studied and resulted in ideal $NO_x$ reduction performances. Recently, supported silver oxide-based catalysts have been reported as having a high potential ability for HC-SCR of NOx. Moreover, in

the presence of water vapor, the Ag/$AL_2O_3$ catalyst also showed high activity, while the conversion of $NO_x$ to $N_2$ on CO/$AL_2O_3$ and $AL_2O_3$ catalysts was highly decreased. Supported rare oxides and noble metals were also studied. Most of them were not active at low temperatures (<400°C) (Nigel, 2007; Reşitoglu, 2015; Simbarashe, 2010). For more effective catalysts, supported transition metals or metal oxides of ,e.g Fe, Cu, Ni, V, Mn, may be used for catalytic $NO_x$ decomposition. Among Ce,V ,Cu and Fe-oxides, $CuO/AL_2O_3$-$PO_4$ catalyst showed the highest NO conversion. $CuOx/Al_2O_3$-$PO_4$ prepared by sol-gel method showed high NO conversion at temperatures (350-400°C). VOx-containing catalysts also showed highest selectivity for $N_2O$, whereas $CuOx/Al_2O_3$-$PO_4$-SG and 2CeOx showed lowest $N_2O$ selectivity(Jasmeet,2005).

### 3.2.6.5. Things to consider in choosing an HC-SCR catalyst:

The catalyst of choice should provide a high performance over a wide window of temperature; selective catalyst for HC-SCR should have some acidity from the support, an adequate active phase (Cu,Co), silver (or a mixture of materials). For a high efficiency, and low sensitivity toward deactivation,we can use some noble metals or Sn (Jasmeet,2005).

## 3.3. Objectif of the study:

The objective of this study was to study the effects of a silver based (Ag-Cu) catalyst with an Ethanol as a reductant on the $NO_x$ conversion ratios in a diesel engine connected to a performance test that is equipped with a DOC, and a HC-SCR . Throughout the experiments, many test parameters were evaluated such as: the space vcelocity, the loading on the engine, and the amount of ethanol/water mixture.

# 4. LITERATURE REVIEW

In this section, previous papers on the subject of of diesel engines' emissions regulations, with an emphasis on NOx reduction and Hydrocarbon selective catalytic reduction have been analyzed and reviewed.

Wilson et al suggested platinum(Pt) supported on multiwalled carbon nanotubes (MWCNTs) as a dual catalyst system for the Selective Catalytic Reduction of NOx with hydrocarbons (HC-SCR) at low temperatures. MWCNTs were prepared via a floating catalyst chemical vapor deposition method. $Pt/Al_2O_3$ was prepared by incipient wetness impregnation of $Al_2O_3$ with aqueous $[Pt(NH_3)_4](NO_3)_2$. catalysts were also prepared by supporting Pt on activated carbon and alumina. Metal deposition on the fMWCNT support was verified by STEM and TEM observations. Pt/fMWCNTs catalyst exhibited superior NOx reduction activity to the 2 wt.% Pt/MWCNTs and $Pt/Al_2O_3$ catalysts with propene as a reductant;while the pristine MWCNTs-based formulation and the reference catalyst reached NOx conversion maxima of 45% at 230°C, the fMWCNTs supported catalysts achieved a NOx conversion maximum of 55% at 200°C. MWCNTs-based formulations showed a higher resistance to oxidation than their activated carbon-supported counterparts, rendering Pt/fMWCNTs a promising low temperature HC-SCR catalyst. The use of a 3:1 Pt–Rh alloy as the catalytically active phase was found to be able to improve the performance of fMWCNTs-supported formulations (Eduardo et al.,2011 ).

Song et al investigated the effects of adding hydrogen on the efficiency of NOx reduction via HC-SCR in both laboratory and engine tests. They used reductants like,propene, heptane, and dodecane as reductants to determine the effects of different chain lengths and chemical structures. the effects of hydrogen addition were significantly influenced by characteristics of the fuel, including the chain length and the structure, and longer chains. The hydrogen was introduced to maximize the efficiency of NOx reduction at low temperatures (245-315°C). They

found that propene, heptane, and dodecane had NOx reduction efficiencies in the Ranged from 20-24%, 9-35%, and 16-20%, respectively. A 2.5 wt.% $Ag/A_{l2}O_3$ catalyst was prepared with a honeycomb monolith support with Ag catalyst loading of 60 $g/ft^3$. The catalyst was supported with activated $Al_2O_3$, and they used boehmite to obtain a high Ag dispersion. The catalyst was calcined at 550 °C in air. With the addition of hydrogen, the efficiency of NOx reduction was the largest with dodecane (58% at 315°C). In the engine tests, diesel fuelwas introduced to the exhaust gases as the reductant, and a maximum efficiency in NOx reduction of 79%was achieved at 315°C, and an efficiency in NOx reduction of 76% was attained at 245 °C(Hyerim and Soonho, 2015 ).

Granger et al found that Bimetallic catalyst Ag–Au supported on high surface area alumina prepared by successive impregnation method had highSCR activity when pretreated in hydrogen at 250 °C compared to pretreatment at 500°C in $H_2$ or air. They also found that The SCR activity of bimetallic AgAuAl catalyst was higher compared to corresponding AuAl and AgAl catalysts after ageing(Pavan,2015).

Sasaki et al investigated the activity of single and two component catalyst systems consisting of a partial oxidation catalyst and a reduction catalyst ($Ag/Al_2O_3$) in a SCR system. The single component $Ag/A_{l2}O_3$ catalyst showed a maximum NOx conversion of 28% at 400°C with n-decane. The composite catalysts, Zn/ZSM-5–$Ag/Al_2O_3$ combination led to the most increase in NOx conversion; a combination of 17 mg of $Ag/Al_2O_3$ and 33 mg of 5%Zn/ZSM-5 led to the most active catalyst showing a maximum NOx conversion of about 67% at 400°C. It was identified that the n-decane can be more effectively converted on Zn/ZSM-5 to smaller hydrocarbons (such as ethene, propane and propene) intermediates and the in situ generated intermediates are effectively utilized on $Ag/Al_2O_3$ for NOx reduction(Asima et al.,2013).

Guangzhi et al found that The 2 wt% $Ag/Al_2O_3$ catalyst showed the best activity for $H_2$-$C_3H_6$-SCR, with excellent water resistance over the whole

temperature range. But adding water vapor to the 2 wt% $Ag/Al_2O_3$for $H_2$-$C_3H_6$-SCR, inhibited the formation of inert formate during the $H_2$-$C_3H_6$-SCR ,and thus increase NOx conversion at low temperatures(Guangyan et al.,2017).

Gunnarsson et al investigated the activity for lean NOx reduction over sol-gel synthesized silver alu-mina ($Ag/A_{l2}O_3$) catalysts, with and without platinum doping, using ethanol (EtOH), EtOH/$C_3H_6$andEtOH/gasoline blends as reducing agents. The results showed that pure $Ag/A_{l2}O_3$ catalysts display higher NOx reduction and lower light-off temperature as compared to the plat-inum doped samples. The 4 wt.% $Ag/Al_2O_3$ catalyst displayed 100% reduction in the range 340–425°C, with up to 37% selectivity towards $NH_3$. These results were also supported by DRIFTS (Diffuse reflection infraredFourier transform spectroscopy) experiments. For future experiments, they suggested that The high ammonia formation could, in combination withan $NH_3$-SCR catalyst, be utilized to construct a NOx reduction system with lower fuel penalty(Fredrick et al.,2017).

Westermann et al investigated the effects of different metal promoters (Pd 0.24%, Co 1.03%, Ag 3.00%) on the activity of novel sulfated ceria-zirconia catalysts for EtOH-SCR, they found that the Pd and Co promoters are mainly present on the acidic support as highly dispersed entities of structure [(MO)n…H]+ in co-existence with MOx/M0 clusters. For the Ag promoter, these species probably coexist with a new $Ag_2SO_4$ cristalline phase, which decomposes above 425 °C under SCR conditions, resulting in the partial deactivation of the silver catalyst.From the detailed analysis of the specific gas profiles recorded during TPSR and steady-state experiments, it was deduced that the metal promoters have only a discrete effect on EtOH-SCR activity, often negative and sometimes positive, by only modifying some of the reaction pathways in the global SCR mechanism. Also,a peculiar effort was carried out in order to elucidate the complex network of reactions occurring during EtOH-SCR, using gas-phase and DRIFTS data(Fredrick et al.,2017).

Evdou et al prepared Ag-based catalysts using the dry impregnation technique. These Ag-based catalysts supported on unpromoted or Ce promoted g-alumina were studied for the selective catalytic reduction (SCR) of NOx with various reductants ($C_3H_6$, $CH_4$ and CO, $C_2H_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, 1-$C_4H_8$ and $C_4H_6$). Among $C_3H_6$, $CH_4$ and CO used as reducing agents, $C_3H_6$ has the higher reducing activity. Higher concentrations of the optimum reductant (1-$C_4H_8$) significantly improved the deNOx performance, achieving over 80% NOx reduction and an interestingly broad active temperature window (300–550°C)(Iliopoulou et al.,2004).

James et al compared the performance of two model SCR catalysts; 5% Cu/ZSM-5 and 2% $Ag/Al_2O_3$ under different operating conditions. They found that With *n*-octane as a model hydrocarbon, the maximum NO*x* conversion for 2% $Ag/Al_2O_3$ (~ 90% at 400°C) was higher than that for 5% Cu/ZSM-5 (~ 60% at 350 ◦C). The Ag catalyst was more active at temperatures of 350°C and above, though the 5% Cu/ZSM-5 catalyst was substantially more active at 300°C. The 2%$Ag/Al_2O_3$ catalyst was also substantially more active than 5% Cu/ZSM-5 after LHA at 700°C. The activity of the Cu/ZSM-5 catalyst was not significantly affected by the nature of the hydrocarbon species, whereas the Ag catalyst showed a strong dependence. The Ag catalyst displayed poorer low-temperature activity with propene than with longer chain hydrocarbons, such as Decane. The Ag catalyst was strongly deactivated by sulphur. The Cu/ZSM-5 catalyst was much more resistant to chemical deactivation. The Ag catalyst was strongly deactivated by sulphur. The Cu/ZSM-5 catalyst was much more resistant to chemical deactivation(Valerie et al,2005 ).

Hilden et al have developed A plasma-assisted NOx SCR reduction system in diesel engine exhaust using reformed diesel fuel as the source of reductants. NOx reduction performances of the system were evaluated in a sidestream connected to the main exhaust stream of a 4.9L, 6-cylinder Isuzu diesel engine dynamometer system. The results were as follows:The performance of the

OHC/SCR process for NOx reduction indiesel engine exhaust had been validated in a series of sidestream engine dynamometer tests. Both (BaY + CuY) and (BaY + Ag/alumina) dual-bed catalysts worked well for NOx reduction via the OHC/SCR process. The optimized deNOx efficiency of diesel fuel reformed by airplasma was better than that of $NH_3$ in the high temperature region, whereas the $NH_3$/SCR was better than any HC/SCR in the low temperature region(Cho et al.,2012).

Leistner et al have studied the ammonia-SCR process with three monolith catalysts: 2.6 wt. % Cu/SAPO-34, 3.1wt.%Cu/SSZ-13, and 2.5 wt.% Cu/BEA with anion-exchange level of 0.20, 0.16 and 0.56 respectively. In order to understand the zeolite type, a couple of reactions were examined: ammonia oxidation,NO oxidation, standard SCR, $NO_2$SCR, and fast SCR. NO oxidation was examined firstly and the result was that Cu/BEA had a higher NO oxidation than the Cu/chabazites. The experiments showed that the small-pore zeolites/silicoaluminophosphates with CHA structure (Cu/SAPO-34 and Cu/SSZ-13) had higher SCR activity at 150°C in Standard SCR conditions, andlower $N_2O$ selection rate than Cu/BEA. But, during fast SCR conditions at 150°C, ammonium nitrate formed over Cu/CHA catalysts, which led to a continuing decrease of NOx conversion. Along with its decomposition temperature, the formation of ammonium nitrate made Cu/BEA more active catalytically than Cu/SAPO-34 or Cu/SSZ-13 at lower temperatures in fast SCR conditions.Also, results showed that ammonium nitrate species had more stability on the small pore zeolites than on Cu/BEA. Ammonia SCR at 150°C and ammonia oxidation at high temperatures had a higher rate on Cu/SAPO-34 than on Cu/SSZ-13 or Cu/CHA Cu-SSZ-13 exhibited the highest ammonia oxidation at low temperatures, where it had a minimum record at 400°C. Additionally,Cu/SAPO-34 registered a higher activity than CU/SSZ-13 at 150°C, despite the fact that Cu/SAPO-34 had less copper in it, which indicated that SCR activity would have been different If copper was incorporated into SSZ-13 or SAPO-34. Results showed also that $N_2O$ formation in standard SCR was higher on Cu/BEA.A result that was attributed to the high

exchange level of copper as well as pores in the structure. The results of this study proved that not only the ion-exchange level had an effect on the activity and selectivity of the SCR process, but also the type of zeolite/silicolaminophosphates (Leistnera et al, 2015).

Lanza and his friend studied three catalysts (pt, Ag on alumina, and Rh) with different temperature range and various space hour velocities that are typical in diesel engines and heavy vehicles. The preparation method of the catalysts was the incipient wetness method with the following catalyst materials: 2wt. %$Rh/Al_2O_3$,2wt%$Ag/Al_2O_3$, and 2wt. %$pt/Al_2O_3$. $C_3H_6$ concentration was varying between 500 and 2000ppm, NO concentration was 500ppm, and Oxygen was 5% at all times.The results of the experiments were as follows: Silver had the highest conversion rates at 50% the least accepted conditions (high GHSV and Low $C_3H_6$ concentration), and 80% to 100% in other conditions. At temperature range of 350°C and 600°C, the catalyst was active, with more than 80% conversion rates at temperature range of 400-550°C. The reducing agent showed a decrease in amount at the highest temperatures because of propene combustion. Steam didn't have a significant effect on conversion rate, but $H_2$ addition improved the reaction and led to high conversion rates at low temperatures. Platinum and Rhodium gave lower conversions than Ag, but were active at lower temperatures (200-400°C). Steam affected Rh severely, while $C_3H_6$ concentration played a role in affecting Pt performance. For Rh, adding hydrogen showed higher conversion rate without the need to propene, however, with the addition of $C_3H_6$, a little decrease in the performance was observed. Up to 150°C, for Pt, there was an effect like that with silver, but above 150°C, NOconversion wasn't affected much(Lanza et al.,2009 ).

Sui et al investigated the effects of $CeSn0.8W0.6Ox/TiO_2$ catalysts for selective catalytic removal of NO and synergistic catalytic removal of $C_3H_8$ and CO that come from diesel engines exhaust. The catalyst preparation method of a series of $CeSn0.8W0.6Ox/TiO_2$ catalyst samples was the extrusion method; the preparation occurred with various active CeSn0.8W0.6Oxmass loading values of

8%,10%,12%,14%and 16% in accordance with the quality of $TiO_2$, and by using $Ce(NO_3)_3\_6H_2O$ (AR), a $SnCl_4\_5H_2O$ (AR), a $(NH_4)6W7O24\_6H_2O$ (AR), an anatase-type $TiO_2$ (CP). The characterization of these catalysts was done using XRD, BET, $H_2$-TPR, $NH_3$-TPD, $O_2$-TPD and CO-TPD techniques. The results of the experiments showed that 12%-CeSn0.8W0.6Ox/$TiO_2$ calcined at 500°C had the best catalytic removal of NO for $NH_3$-SCR with more than 90% reduction rate at temperature window of 252-456°C with a GHSV lower than 10000 $h^{-1}$. Additionally, the presence of 5(v/v) % $H_2O$ at high reaction temperature didn't affect the activity of the catalyst,which was lower in the presence of 200ppm of $SO_2$ at 361"C where the conversion rate of NO was 94.01%, however, after eliminating $SO_2$ and $H_2O$, the catalytic activity exhibited an improvement. The factors that influenced the results were mass ratios of active compounds,operating conditions, and calcinations temperature. Furthermore, to obtain a good catalytic performance of NO, CO,and $C_3H_8$ removals, promotional factors like redox property,big surface area, and rich surface acidity might be considered(Suia et al.,2017).

Shang et al studied the effects of CO on the catalytic activities of $Ag/Al_2O_3$ using propane as a reductant in NOx reduction. The preparation method of the supported $Ag/Al_2O_3$ catalysts was the conventional incipient impregnation method, with $AgNO_3$ used as a precursor. The catalysts were characterized using Powder X-ray diffraction (XRD) and BET. The results showed that CO didn't show significant effect on the activity of $1Ag/Al_2O_3$for $C_3H_8$-SCR, however, it promoted the activity of Ag catalyst with higher Ag loading. Also, the temperature window of operation of $C_3H_8$-SCR on 5% $Ag/Al_2O_3$ was widened from 425-510°C to 375–545°C, thanks to the presence to CO. CO, however, with its direct positive effect on $C_3H_8$-SCR, didn't have a direct involvement in reducing NO. In situ DRIFTS, it was shown in different feed gases that the presence of CO improved the $C_3H_8$partial oxidation on$5Ag/Al_2O_3$, and resulted in a significant increase of intermediate species of $C_3H_8$partial oxidation, like acetate and enolic species which

boosted the $C_3H_8$-SCR reaction. Also, these enolic species presence could provide another method to remove NOx (Shang et al.,2016).

Xiao et al prepared a series of $CuCl_2$/NaZSM-5 and $CuCl_2$/HZSM-5 samples from high dispersion of $CuCI_2$ into NaZSM-5 and HZSM-5 zeolites. NaZSM-5 zeolite was synthesized by reaction of analuminosilicate gel containing Na and tetrapropylammonium (TPA) cations. These catalysts were characterized by X-ray diffraction (XRD), hexaneisotherms, differential thermal analysis, and IR spectroscopy. The results showed that the samples of NaZSM-5, HZSM-5, $CuCl_2$.NaZSM-5, and $CuCl_2$/NaZSM-5 catalytic activities in reducing NO by propylene at 300°C were low in comparison with ion-exchanged prepared sample of CuZSM-5. Infrared spectroscopy showed that the samples of $CuCl_2$/HZSM-5 and CuZSM-5 exhibited a band at NO conversion as a function of reaction temperature over $CuCl_2$/HZSM-5 that was prepared by the mechanical mixture of HZSM-5 with $CuCl_2\_2H_2O$ ($Cu_2$./HZSM-5.0.048 g/g), After that , it was heated for 24 h at 400°C, $CuCl_2$/NaZSM-5 prepared from the mechanical mixture of NaZSM-5 with $CuCl_2\_2H_2O$ ($Cu_2$/NaZSM-5.0.048 g/g), followed by heating for 24 h at 400°C, and CuZSM-5 that was prepared by ion-exchanged method ($Cu_2$/HZSM-5.0.024 g/g). The correlation of catalytic data with infrared spectra for $CuCl_2$/HZSM-5, CuCl2/NaZSM-5, and CuZSM-5 samples showed that the catalytic sites can be attributed to synergetic effect of copper species and protons(Xiaoa et al,1999).

M. Abu-Jrai and his friends investigated the effects of tri fuel($CH_4$,$H_2$,and ULSD) with various gaseous fuel mixtures operating under real exhaust gas conditions on the emissions of the engine, the characteristics of the combustion, and selective catalytic reduction(SCR) after treatment at low,medium,and high engine loads. The catalyst used during the study was 1% $Pt/Al_2O_3$. It had an hourly gas space velocity between 65,000 $h^{-1}$ to 85,000 $h^{-1}$ and as a catalyst support a cordierite honeycomb monolith was used. The preparation method of the catalyst was the standard impregnation method using platinum nitrate solution with alpha-

alumina (a-$Al_2O_3$) phase. Pt/$Al_2O_3$-SCR reactor had been operated at various exhaust gas temperatures. Results showed that the gaseous fuels($CH_4$ and $H_2$) have the same change in the combustion process, and they both minimized the rate of heat release and in-cylinder. There was, however, a significantincrease of the premixed combustion phase and a considerable decrease of the the whole combustion period at high engine loads. Also, at high engine load,fuels with bigger amount of $CH_4$ had a tendency to reduce formation of NOx, however, for fuel with so much $H_2$ content had a tendency to decrease PM emissions formations, additionally, Tri fuel combustion with 50:50 mixture of fuel had lower BSFC in result as compared to the other ratios, and for that reason, the optimal engine efficiency. Under real diesel exhaust gas, hydrocarbon-SCR showed satisfying results in reducing NOx emissions in temperatures window of 180-280°C(Abu-Jrai et al.,2017 ).

# 5. MATERIALS AND METHODS

In this section, the ceramic materials used in preparing the catalyst were defined and explained along with, the chemicals used in coating the catalysts, the preparation steps of the catalyst, The specifications of the instruments used to analyze the structural and chemical properties of the catalyst, The experiment setup for testing the catalyst in real conditions, the technical specifications of all the instruments related to the setup experiment, and finally, the electronic equipments and programs that were used throughout all the conducted experiments.

## 5.1. Catalyst preparation:

The catalyst was prepared using the impregnation method ; it is a method that includes impreganating a support with precursor solutions, drying,calcination,and evaporation. First, the Cylindrical Cordierite was sliced to desired dimensions (Figure 5.1) at Cukurova University automotive engineering's laboratory. Next, The Cordierite (Figure 5.1) was weighed using a digital weighing device RADWAG AS 220 .R2 (Figure 5.8) and it weighed approximately 92.88g. Soon after, It was put into the oven for an hour at a temperature of 110°C to make it rigid and dry. Next 5,2g of copper crystals,and 10,1g of silver powder were wieghted to later be mixed and stirred with a 500ml of distilled water (Figure 8) via a Sonic Vibra-Cell VC 750 ultrasonic processor for 20 minutes at a frequency of 20KHz; nanoparticles of silver and copper were mixed with distilled water with pulsing time 10 seconds on 10 seconds off and 40% amplitude in order to get a homogenous solution.The next step consisted of impregnating the cordierite in the homogenous solution repeatedly. After getting the cordierite drenched well in the solution,It was left to be dried for a while and then it was put back in the oven for one hour at a temperature of 110°C to completely dry out. Next,The cordierite was sintered for five hours at a temperature of 600°C. After

the sintering process the catalyst weighed approximately 105 g and the catalyst was ready to be used in the experiment.

### 5.1.1. Cordierite Specifications:

In the preparation of the catalyst, a ready cordierite ($2Al_2O_3$-$5SiO_2$-$2MgO$) with a monolith honeycomb as a support was used (Figure 5.1) with the following dimensions: 103x130mm and a 400 cpsi square pores. When compared with other supports, the monolith stands out because of its thermal expansion rate, its superior hydrothermal stability, and low cost, and hence, its use in the experiments (Wang et al., 2015 ).

Figure 5.1. Monolith honeycomb Cylindrical Cordierite

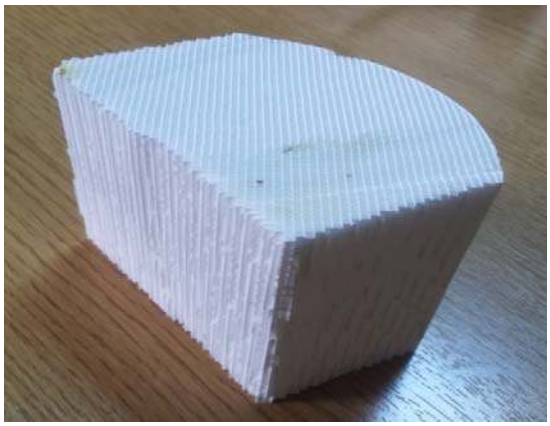

Figure 5.2.Cut cordierite to be used in the catalyst preparation


Figure 5.3. Silver, Copper, and distilled water

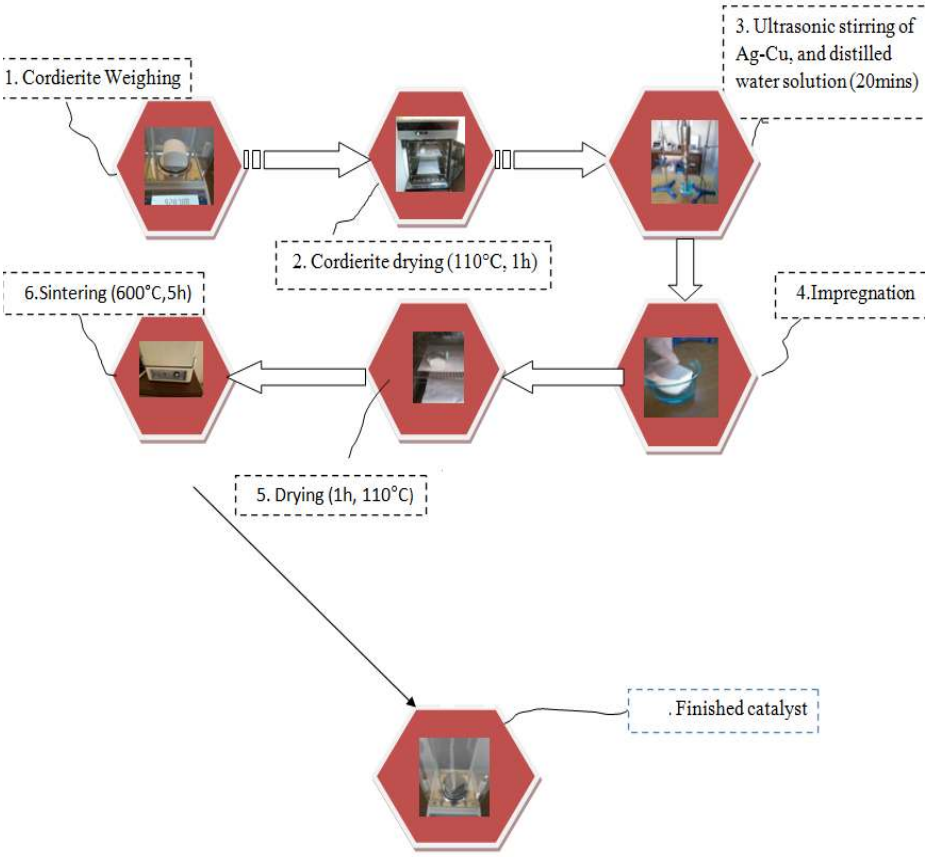


Figure 5.4. Catalyst Preparation schematic

## 5.2. Catalyst characterisation equipments and technical properties:

In thise section, the technical specifications of the machines used to analyse the catalysts ( XRD, BET, and SEM ) were explained as follows:

### 5.2.1. X-ray diffraction(XRD):

A technique was used to identify the molecular structure of a crystalline material by diffracting x-rays into the sample. By obtaining interference patterns, An XRD analyzer can reflect lattice structures by modifying the incidence angle of the X-Ray beam. The X-RAY DİFFRACTOMETER (XRD) used in our thesis wasthe PANalytical EMPYREAN XRD (Figure 5.5) available in the Cukurova univeristy's central research laboratories.

Figure 5.5. The PANalytical EMPYREAN XRD

Table 5.1. The PANalytical EMPYREAN XRD

| | |
|---|---|
| Tube | X-Ray tube,CU-Ka |
| Voltage range[KV] | 20-50 |
| Flow range[MA] | 5-60 |
| Goniometer diameter[mm] | 480 |
| Goniometer geometry | Perpendicular,therta-therta, and alfa-1 |
| Smallest size of step | 0.0001°( θ/2θ). |
| Scanning speed | 0.0001°/minute |
| Angle-to-angle passing speed | 500°/minute |
| Maximum angle | 111< 2 θ <168° |
| Detector | high-speed pixel-based |
| Maximum counting capacity | 1x106 signal/sec |
| Minimum pixel space | 70 micron x 70 micron |
| Fixed snapshot in angular field | 4° (2θ) |
| Mapping | 2D |
| Model | Bragg-Brentano optic model |
| Collimator | Cross-slit |

**5.2.2. BET Analysis:**

Brunauer-Emmett-Teller (BET) Surface Area Analysis is a technique that proves determining measures of the surface area,micro and macro pores size, and pores size distribution by physical adsorption method in solid and powder samples at low pressures and with high-resolution.The device used in the experiments was the KELVIN 1042 device which is available at the universities research labs, shown in Figure 5.6:


Figure 5.6. KELVIN 1042

Table 5.2. KELVIN 1042 technical properties

| | |
|---|---|
| Gas volume measurement interval | 0.005-20cc |
| Specific are that can be measured(SSA) | 0.01 $m^2/g$ |
| Pore size[nm] | 2-200 |
| Ability | Can work with 6 sample in one cycle |
| Degassing Temperature | 35-350°C |
| Analyses period | 15 minutes(single point) |

**5.2.3. SEM analysis:**

The scanning electron microscope (SEM) is a technique that can do analysis of solid specimens,namely,any conducting sample that doesn't have liquid properties, metals,textiles,fibres,and plastic polymers; also, samples that are not conductive can be coated with very thin (2Å/second) conductive material and be analyzed. This process works by focusing a beam of high- energy electrons to produce different signals at the surface of the specimen. The signals obtained from electron-sample interaction provides information about the specimen like its

morphology (texture),crystalline structure,orientation of the materials available in the sample, and chemical composition. In general, the data gets collected in one area of the surface of the specimen,and spatial variations are shown in a produced 2-dimensional image.In this thesis, FEI Quanta 650 Field Emission SEM(Figure 5.7 ) available at the cukurova university's central research labarotory was used.


Figure 5.7. FEI Quanta 650 Field Emission SEM

The technical properties of the device are:Microscop's resolution; in high vacuum,in 30kV 1.2nm(SE),in 1KV 3nm(without slowing down the electron)(SE),in Low vacuum,30kV 2nm(SE); high vacuum SE and four department BSE detector that can be summoned back;high vacuum incolumn SE and BSE detector;X-Ray energy distribution spectrometery;GSED (for ESEM mode)detector;STEM detector that can be called back;BSE detector that can work in low vacuum; voltage of acceleration, 100V-30kV;probe flow,100nA;amplification:6-1.000.000 x;camera navigation.

### 5.3. Chemicals properties of materials used in Catalyst preparation:

#### 5.3.1. Ethyl Alcohol:

The central theme of this thesis was to experiment with the effects of ethyl alcohol as a Hydrocarbon reductant in reducing the NOx emissions in a HR-SCR system. Ethyl alcohol($CH_3CH_2OH(C_2H_6O)$) also known as ethanol or alcohol or

grain alcohol derives from class of organic compounds with the name alcohols, can be used as a solvent,in synthesizing of different organic chemicals,and also as an additive to gasoline.Ethyl alcohol is the stimulating component in beer and wine [Anonymous 4].Ethyl alcohol can obtained by either fermenting carbohydrates( like the process of producing wine),or by Ethylene($CH_2$) hydration. Pure ethanol is flammable,colorless with the following technical properties:

Table 5.3. Ethyl Alcohol Properties

| | |
|---|---|
| Auto ignition temperature | 422°C |
| Boiling Point | 78.5°C(173.3°F |
| Melting Point | 117.3°C |
| Molecular Weight | 46.069g/mol |
| Specific Gravity(water=1) | 0.79@20°C |
| Vapor density(air=1) | 1.59 |
| Vapor Pressure | 44mm Hg@20°C |
| Evaporation rate | 3.10 |
| Viscosity | 1.19cps@20°C |
| Flash Point | 13°C |
| PH value | Neutral |

Ethyl alcohol has a delicate odor and a burning taste. It is toxic and modest amounts of intake can be stimulating while high amounts of intake can affects sound judgement and reason, it makes people addictive and diseased with alcoholism. In the body,Ethanol is converted to acetaldehyde first and then to water and carbon dioxide, at the rate of 15ml/ hour, which is the equivalent to aintake diet of a 100 calories (Anonymous 4 ,Anonymous 5).

### 5.3.2. Silver Nitrate (AgNO3

Silver compound(salt) that is used in preparation of many types of silver derivatives. Brand of the chemical: Merck; The physical properties of silver nitrate are: density of 4.35g/ml, boiling point of 440 °C, melting point of 210°C, molecular weight of 169.872 g/mol (Anonymous 6).

### 5.3.3. Copper(II) Nitrate Trihydrate($CuH_2N_2O_7$):

It is a crystalline dark blue powder with molecular weight: 241.6g/mol; melting point: 1083°C; Boiling point: 2567°C; Density: 8.89g/$cm^3$ at 20°C (Anonymous 7).

## 5.4. Technical properties of the devices used in catalyst preparation:

This section explained the properties and technical specifications of all the laboratory devices used in catalyst preparation.

### 5.4.1. RADWAG AS 220 .R2:

Table 5.4. RADWAG AS 220.R2 technical properties

| | |
|---|---|
| Maximum capacity | 220g |
| Minimum load | 10mg |
| Tare range( T) | 220g |
| Readability (d) | 0.1mg |
| Operating Temperature | 10°-+40°C |
| Power Supply | 12/16VDC |
| Stabilization time | 2s |
| Weiging pan dimensions | 100mm |
| Net Weight | 5.3Kg |

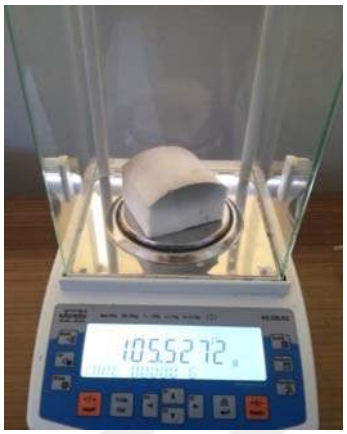


Figure 5.8. RADWAG AS 220 .R2

### 5.4.2. Ultrasonic Processor:

The technical properties of the vibra-Cell V750 ultrasonic processor are given below:

Table 5.5. Vibra-Cell V750 ultrasonic processor technical properties

| | | |
|---|---|---|
| **Power Supply** | **Net power output** | **750watts** |
| | Frequency | **20KHz** |
| | Dimensions: (H x W x D): | **235 x 190 x 340mm** |
| | Weight | **6.8kg** |
| **Sealed converter** | Part No: | **Piezoelectric lead zirconatetitanate cry** |
| | Diameter | **63.5mm** |
| | Length | **183mm** |
| | Weight | **900g** |
| | Cable Length: | **1.8m** |
| **Standard probe** | Tip Diameter | **13mm with threaded end replacable tip** |
| | Processing capability: | **10ml to 250ml** |
| | Length: | **136mm** |
| | Weight | **340g** |
| | Material | **Titanium alloy Ti-6A-4** |

Figure 5.9. vibra-Cell V750 ultrasonic processor

### 5.4.3. Sintering Oven:

The sintering process of the catalyst at 600°C for five hours was done using the Protherm furnace Model PLF 110/6 (figure 5.10) with the following specifications: Maximum Temperature: 1100(°C);Continuous Operating Temperature (°C):1050; Volume (L):7.0; Inside Measurements (HxWxD) (cm): 14x20x25; Outside Measurements (HxWxD) (cm): 65x55x58; Power:1350W; voltage:220v; Phase:1

Figure 5.10.Protherm furnace Model PLF 110/6

### 5.4.4. Drying Oven:

During the catalyst preparation we did a drying of the catalyst two times which was done using the Memmert BAIC oven UNB 500 with the technical specifications shown in Table 5.6:

Table 5.6.Memmert BASIC oven UNB 500 Specifications

| Model | UNB 500 |
|---|---|
| Chamber width A[mm] | 560 |
| Chamber height B[mm] | 480 |
| Chamber depth C[mm] | 400 |
| Oven width D[mm] | 710 |
| Oven height E[mm] | 760 |
| Oven depth F[mm] | 550 |
| Chamber volume[litre] | 108 |
| Weight[kg] | 50 |
| Power[W] | 2000 |
| Max number of trays | 5 |
| Max.load per tray[kg] | 30 |
| Total load per oven[kg] | 60 |
| Ambient conditions | Ambient temperature 5°C to 40°C |
| Setpoint temperature range | 20° C to nominal temperature |
| Setting accuracy | 0.5°C |
| Indication resolution | 0.5 °C |
| Nominal voltage[V] | AC 230 |

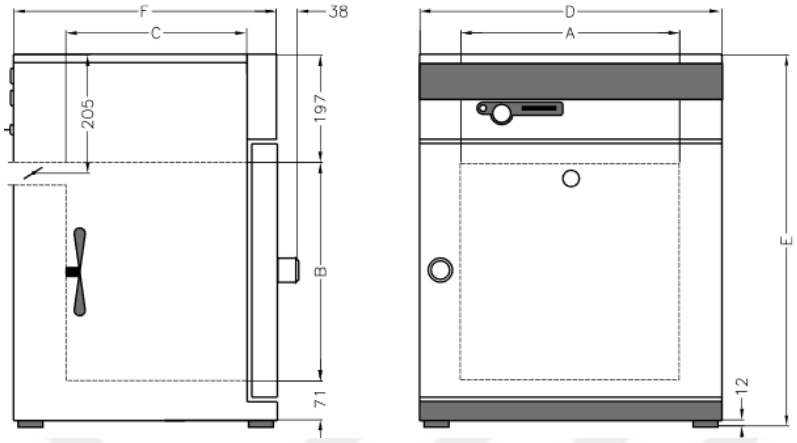


Figure 5.11. Oven Cross sectional drawings

**5.5. NOx emissions measurement test system:**

In this section, the components and the installment processes of the Nox measurement system were explained, including the engine, the heater, the loading system, the compressor, the matlabsimulin computer program that was employed,the loading mechanisms, and the emissions control system, and its working mechanisms.

**5.5.1. Performance test system overview:**

To test the effects of Ethanol as a reductant and the silver-copper catalyst on the efficiency of NOx reduction, an AKSA diesel engine (Figure 5.17) available at the automotive department's laboratory was used, and to load the engine, a 10KW electric loading system (Figure 5.20) was used in tandem with it. The loading amount pulled by the loading system was kept constant by means of measuring the voltage and the electric current intensity. The test system generally comprises an engine, a loading system, and a specifically designed performance test system (Figure 5.12). To determine the exhaust gas flow rate aboard the system, an orifice plate was mounted onto the exhaust system. In order to adjust the exhaust gas temperatures, a heater, too, was included in the system. Temperatures

were measured using k-type thermocouples temperature sensors (Figure 5.11), installed One before DOC, and one after DOC in the exhaust system. NOx emissions reduction rates were monitored using two Continental model NOx sensors (Figure 5.11). To extract data from these two sensors, a program was written in accordance with the CAN J1939 protocol, and using a PCAN-USB, the data extracted was recorded into the computer. To ensure the NOx reduction in the SCR system, the process of reductant spraying was composed of a multi-point(6 pores) injector and a pump that were controlled using a microprocessor hardware and software. Reductant spraying was monitored electronically using a matlab Simulink program on the computer that took measures of the spraying flow rates, an Arduino MEGA 2560 microprocessor (figure 5.14), and I/O carts. While the injectors pulse width modulation (PWM) was being operated under control, the pump was also, at the same time, being operated with an On-Off control mode. The space velocity of the gas flow; space velocity [SV ($h^{-1}$)] is the ratio of exhaust-gas volumetric flow [Vf ($m^3/h$)] to catalyst volume [Vc ($m^3$)] (Reşitoglu, 2015) was measured using amanometer with an orifice plate.

The experiments were done employing several variations like two variations of space velocity values (20,000$h^{-1}$, 40,000$h^{-1}$) , four different engine loads (1 KW,2 KW, 3KW, and 4 KW), and finally reductant spray ratio variations (4% distilled water to 96% Ethanol, 100% Ethanol). To determine the efficiency and performance of using the prepared catalyst with the hydrocarbon reductant in reducing NOx emissions, especially at low temperatures, NOx emissions rates were measured in the temperature window of 170-260°C. Each experiment was conducted more than one time to ascertain the data obtained.

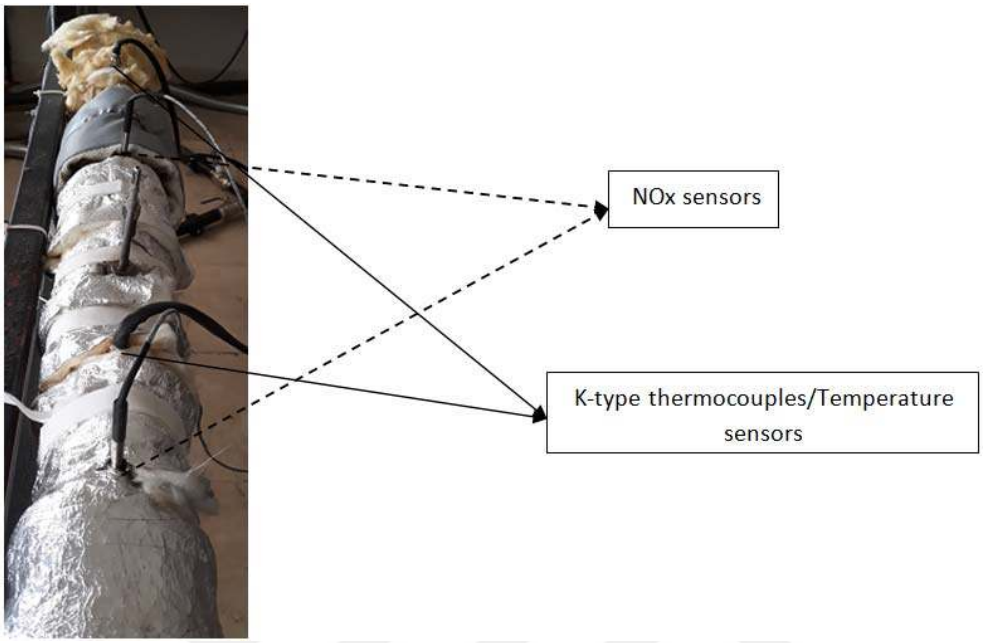


Figure 5.12. Exhaust pipe showing the Nox sensors and the K-type thermocouple

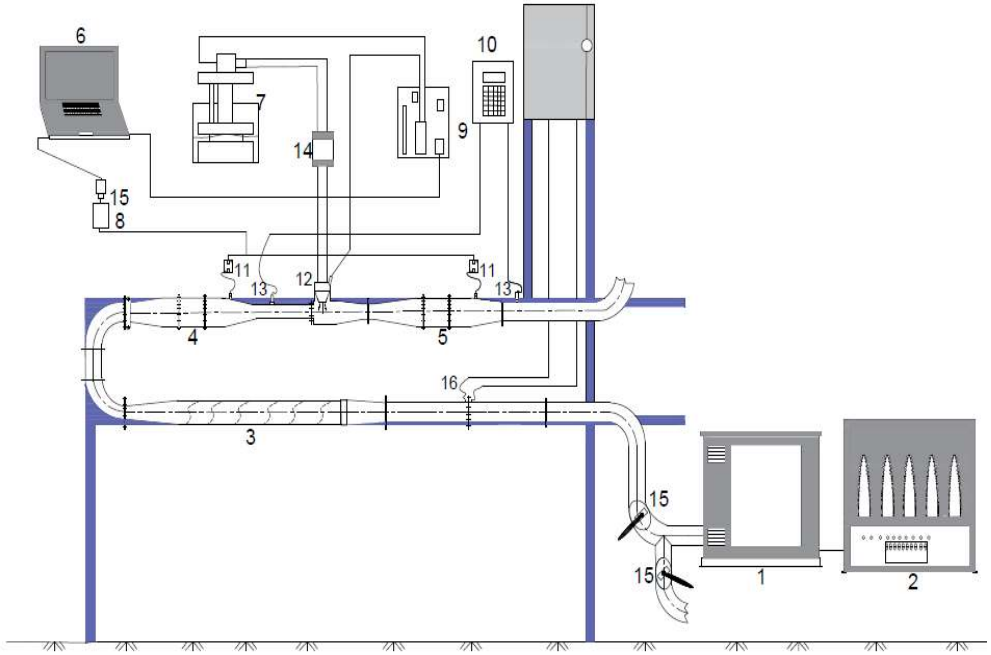


Figure 5.13. Layout of the experiment

Figure 5.12. Layout of the experiment schematic view (1-Engine, 2-Electric loading system, 3-exhaust gas heating department, 4-DOC (Diesel oxidation catalyst), 5-SCR (selective catalytic reduction),6-SCR control unit, 7-reducing agent (Ethanol), 8-24V power source, 9-injector spraying control unit, 10-Dijital temperature measurement device, 11-NOx sensor, 12-injector, 13-temperature sensor, 14-reductant liquid filter, 15-manual valve, 16-Orifice Plate).

### 5.5.2. Test system components technical properties:

In this section, the technical properties of the appliances used in test performance were explained.

#### 5.5.2.1. Nox Sensors:

Throughout the experiment NOx emissions rate were the most important parameters to keep up with and measure in the experiments. The NOx gas emissions changed according to the engine working conditions. In the experiment setup, Two NOx sensors were placed one before the SCR catalyst and one after the SCR catalyst; the first sensor was used to measure the NOx emissions before spraying the ethanol reductant, and the second sensor was placed to measure the NOx emissions after the reductant spray, due to the fact that a comparison can be realized. In the figure (5.14) a Continental UniNOx sensor is shown, the sensor communication was done according to CAN J1939 protocol.

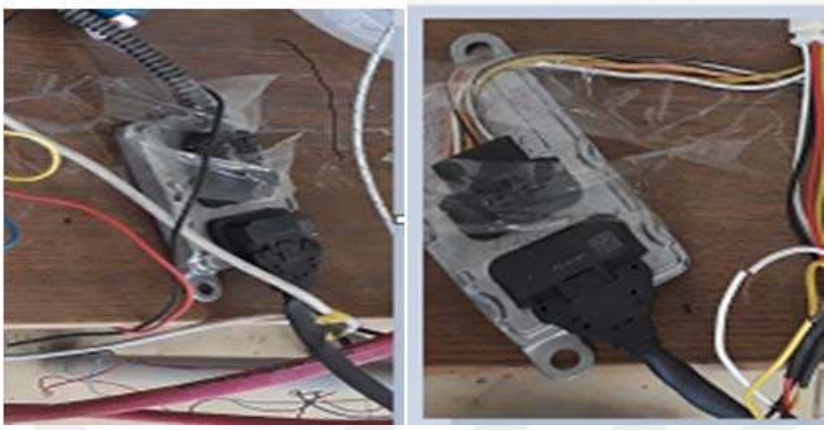

Figure 5.14. Continental NOx sensors

**5.5.2.2. Arduino MEGA 2560:**

Arduino MEGA 2560 was uploaded with a program (code) and used together with matlab simulink on the computer to control the pump flow and speed of the reductant spraying. The technical specifications of which are:

Table 5.7.Arduino MEGA 2560 Specifications

| **Microcontroller** | **ATmega2560** |
|---|---|
| Operating voltage | 5V |
| Input voltage(recommended) | 7-12V |
| Input Voltage(limits) | 6-20V |
| Digital I/O pins | 54(of which 14 provide PWM output) |
| Analog Input pins | 16 |
| DC current per I/O Pin | 40Ma |
| Dc current for 3.3V Pin | 50Ma |
| Flash memory | 256kb of which 8KB used by bootloader |
| Spam | 8KB |
| EEPROM | 4KB |
| Clock Speed | 16MHZ |

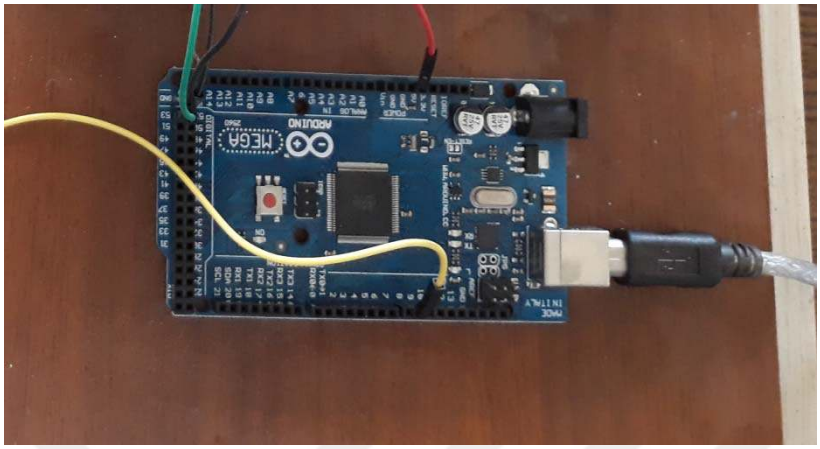

Figure 5.15. Arduino MEGA 2560

**5.5.2.3. PUMP:**

A gasoline pump available at the Cukurova University Lab was used in the experiments to Spray water with a multi-points (six pores) reductant injector. The pump is connected to an Arduino MEGA 2560 which in turns is connected a matlab program to monitor the spraying flow.

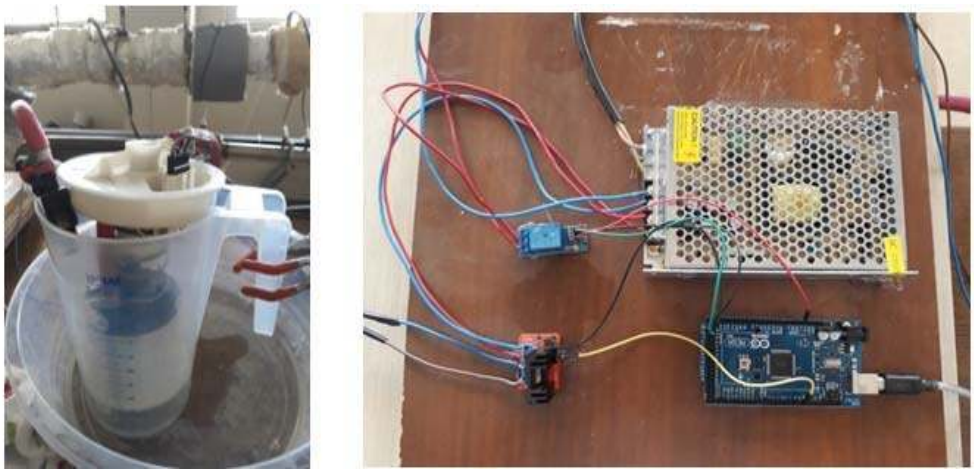

Figure 5.16. Pump connected to an Arduino

**5.5.2.4. Generator:**

To test the $NO_x$ reduction system and conduct our lab experiments an AKSA A2CRX08 2-cylinder V-type diesel engine with a bore of 80mm and a stroke of 79mm was used. The technical specifications of the motor are shown in table below:

Table 5.8. AKSA A2CRX08 technical properties

| Model | APD 12EM |
|---|---|
| Prime frequency(Hz) | 50 |
| prime power(KVA) | 8.8 |
| Stanby power(KVA) | 9.6 |
| Nominal voltage(V) | 230 |
| Nominal flow(A) | 38 |
| R.P.M(r/min) | 3000 |
| PHASE | 1p |
| Power factor($\cos^{\varphi}$) | 1 |
| Warning mode | Brushless capacitor |
| Oil capacity | 2.3 |
| Water capacity | 6.4 |
| Fuel tank capacity | 15 |
| Fuel consumption(L/h) | 4 |
| Battery voltage | 12V DC |
| Dimensions(mm) | L=1158 W=775 H=1017 |
| Cylinder volume($cm^3$) | 794 |
| Stroke(mm) | 79 |
| Cooling mode | Water |
| Compression ratio | 23/1 |

Figure 5.17. AKSA generator

### 5.5.2.5. Orifice plate and menometer:

A manometer and an orifice plate were installed in the system and connected to the exhaust pipe to calculate the hourly space velocity using Bernouillie's equation. The manometer is filled with water and the desired space velocity ( 20,0000,40,0000$h^{-1)}$ corresponds to a certain water level difference in the tube measured by a micrometer.

Figure 5.18. Manometer with an orifice plate

**5.5.2.6. Emissions measuring equipment:**

To measure exhaust gas emissions from the engine at rest, an MRU DELTA 1600-V was used with the following technical properties:

Measuring Ranges and other data;

- CO : 0 ... 10 %
- $CO_2$ : 0 ... 20 %
- $O_2$ : 0 ... 22 %
- NO : 0 ... 4.000 ppm
- $NO_2$ : 0 ... 1.000 ppm
- CxHy : 0 ... 20.000 ppm
- Display : 10 - lines, backlit graphical display
- Weight:appr. 10 kg
- Dimensions : 530x490x310 mm

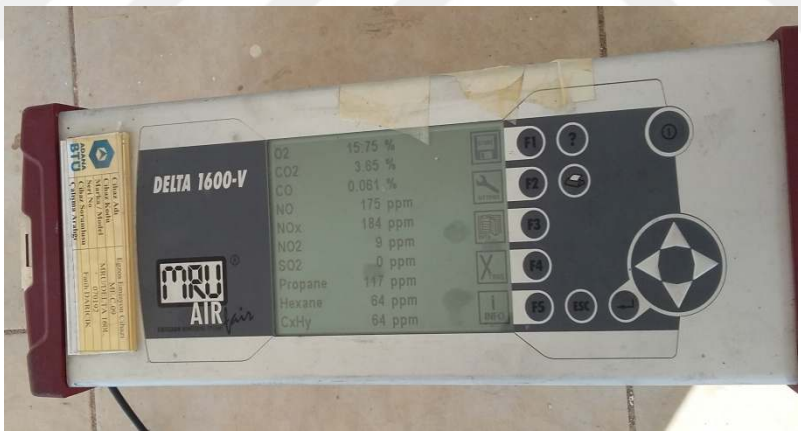


Figure 5.19. MRU DELTA 1600-V

**5.5.2.7. Thermocouple thermometer:**

To measure the temperatures during the experiments a KJTRSE thermocouple thermometer logger 9682 was used with following specifications:

- K temperature range and Accuracy: 200-1370°C;(0.3% rdg +0.7°C)
- J temperature range and Accuracy:200-760°C;(0.3% rdg +0.7°C)
- T temperature range and Accuracy:200-390°C;(0.3% rdg +0.7°C)
- R temperature range and Accuracy:0-1760°C;(0.3% rdg +0.7°C)
- S temperature range and Accuracy:0-1760°C;(0.3% rdg +0.7°C)
- E temperature range and Accuracy:200-736°C;(0.3% rdg +0.7°C)
- Resolution:0.1°C
- LCD size(mm,HxW): 26(H)x45(W)mm
- Operating temp: 0-50°C
- Operating RH%: Humidity<80%
- Storage temp: 20-50°C
- Storage RH%: Humidity<90%
- Dimension(mm,LxWxT): 170x70x40(H)mm
- Weight: 210g
- Battery:AAA batteryx4pcs or 9v adaptör

Figure 5.20. KJTRSE thermocouple thermometer logger 9682

### 5.5.2.8. Electric Loading system:

The motor was loaded using a 10KW loading system available at the automotive laboratory (Figure 5.21). The NOx emissions rates witnessed a significant change among different loads (1KW, 2KW, 3KW, and 4KW).

Figure 5.21. Electric loading system

# 6. RESULTS AND DISCUSSION

In this section, The experimental and laboratory results of Catalyst characterizations (SEM, BET, and XRD), and Performance test results of eight different experiments conducted in the lab in order to study the effect of Ethanol and Silver based catalyst on NOx conversion rates were presented and discussed with an overall conclusion and recommendations for future work.

## 6.1. Catalyst Characterization results:

### 6.1.1. SEM analysis Results:

The photographs seen in Figure 1 and Figure 2 show The SEM images of the cordierite before and after coating with Ag-Cu taken in different scales (5000x and 10000x) and resolutions (5micrometer, 10micormeter). The mapping of the elements on the cordierite is shown in different colors in Figure 3. SEM images of the cordierites represent generally the cross section of nanowires arrangements on the monolith cordierite and show how the nanoscale organization of the cordierite looks like. We can see with the high resolution (10000x) SEM image (Figure 1) how the cordierite is composed of a porous structure. It has been proven that increasing the nanowires coverings of the channel surface of cordierite will increase the surface area, along with the quantity of the active sites.

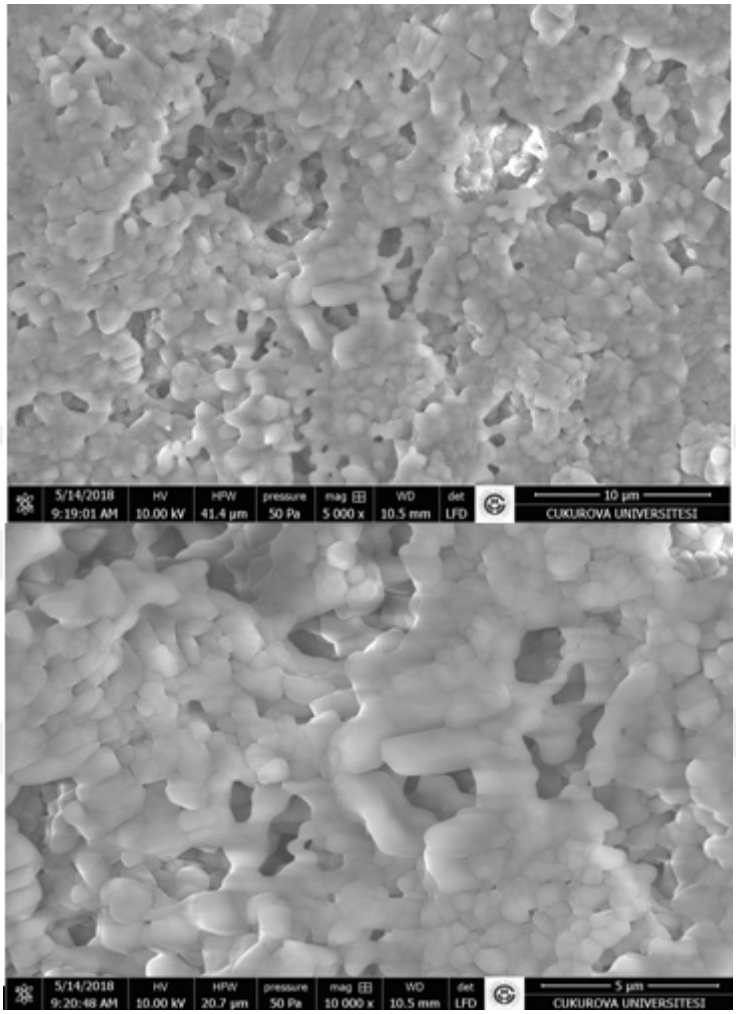


Figure 6.1. SEM images of the cordierite

Figure 6.1 Shows the two SEM images results of the cordierite at 5000x resolution and 10 micrometer(upper image), 1000x resolution and scale of 5 micrometer(lower image)

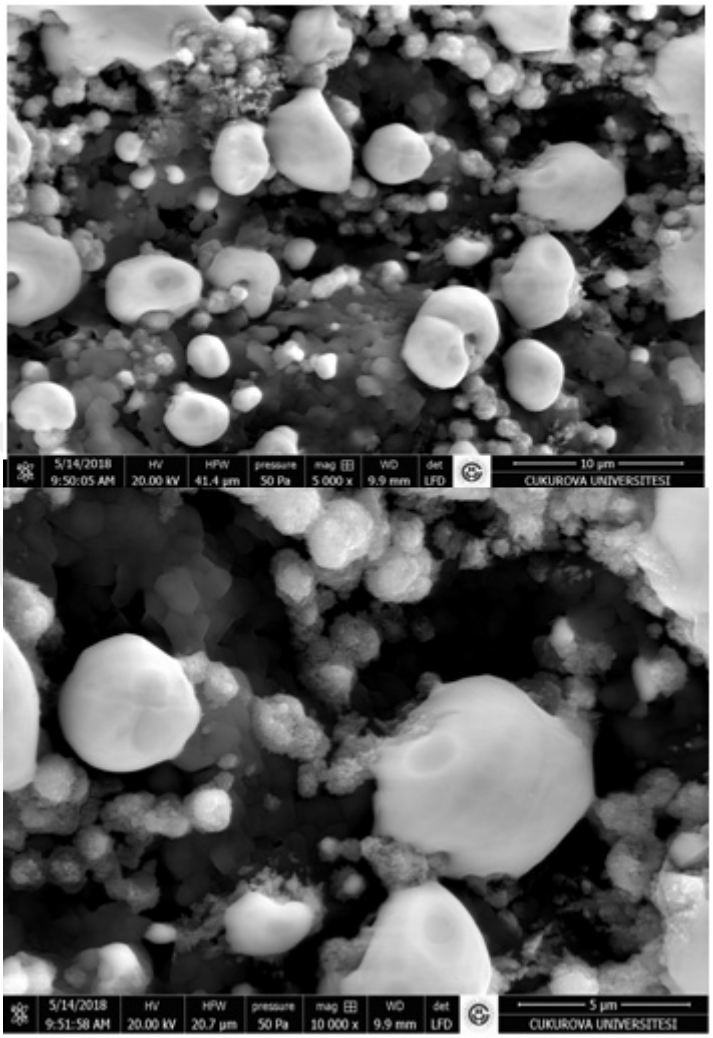


Figure 6.2. SEM images of the prepared catalyst

Figure 6.2 displays photograph of two SEM images of the catalyst, the upper image with a resolution of 5000x and a scale of 10micrometer, the lower image with a resolution of 10000x and a scale of 5 micrometer.

Copper and Silver nanowires are expected to spread across the whole surface of the monolith and the gaps and microwires to be as little in number as possible (Şen et al., 2016). When analyzed, SEM images (figure 6.2) showed how

the coatings homogeneity was spread over the surface of the cordierite, and how the silver and copper nano particles have penetrated the catalyst surface. The high resolution SEM image exhibited some areas with gaps on the surface; It indicates that Copper and Silver crystals might have not been formed in some areas. The white ball shaped things in the image corresponds to the dense concentration of the silver crystals in some areas on the catalyst (Şen et al., 2016). It is worth noting that the gaps available represent a small fraction of the catalyst surface which doesn't affect the efficiency of filtration in the catalyst.

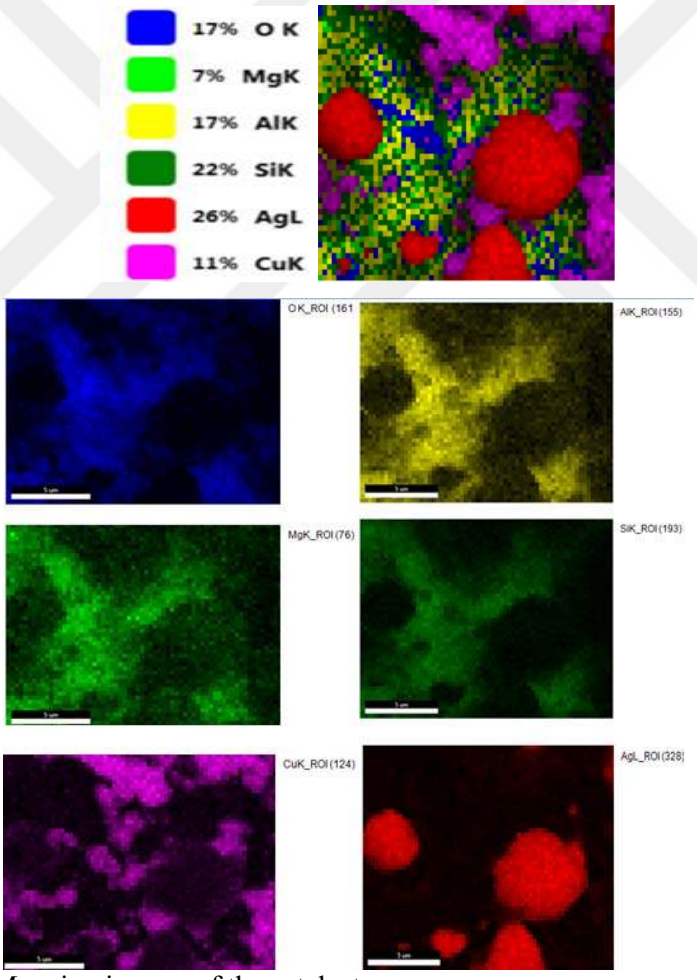


Figure 6.3. Mapping images of the catalyst

In The mapping analysis process of Figure 6.3, the observation of the coating elements (Cu and Ag) that are supposed to exhibit a catalytic activity on the coating surface of the catalyst were distributed evenly or homogeneously on the surface. The red spots in the images corresponds to the silver particles (Ag) and the pink spots to the copper (Cu). In conclusion, the investigation of the analysis done by the SEM device and the results obtained by the microscopic and mapping proved following in check:

-A catalyst with porous structure,
-Coating done homogeneously across the surface,
-Elements whole penetration of the catalyst surface.

**6.1.2. XRD Analysis results:**

The Cordierite ($2Al_2O_3$-$5SiO_2$-$2MgO$) before and after impregnation with aqueous solution of Silver nitrate ($AgNO_3$) and Copper (II) Nitrate Trihydrate ($CuH_2N_2O_7$) XRD's results are shown in Figure 6.4 and Figure 6.5 respectively. Figure 6.4 exhibited an intense peak at 2θ=10°, average peaks at 2θ=22°,27°,29°,and 30°, and low peaks at 2θ=18°,35°,39°,and 55°. This distribution of peaks in the cordierites XRD analysis represented the crystal structure of the cordierite. As for the catalyst prepared, XRD results patterns Figure 6.5 indicated a decrease in peak intensity ( 2θ=10°) as opposed to the intense peak of the raw cordierite, emergence of intense peaks at 2θ=31°,31°,37°, and 41°, and low peaks at 52°,56°, and 58°. The intensification of peaks after impregnation of the cordierite is thought to be attributed $AgNO_3$, and $CuH_2N_2O_7$, added after impregnation.

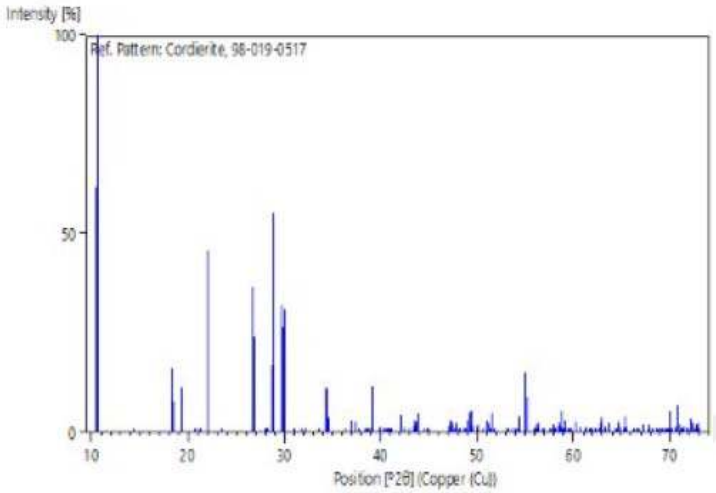


Figure 6.4. XRD results of the cordierite

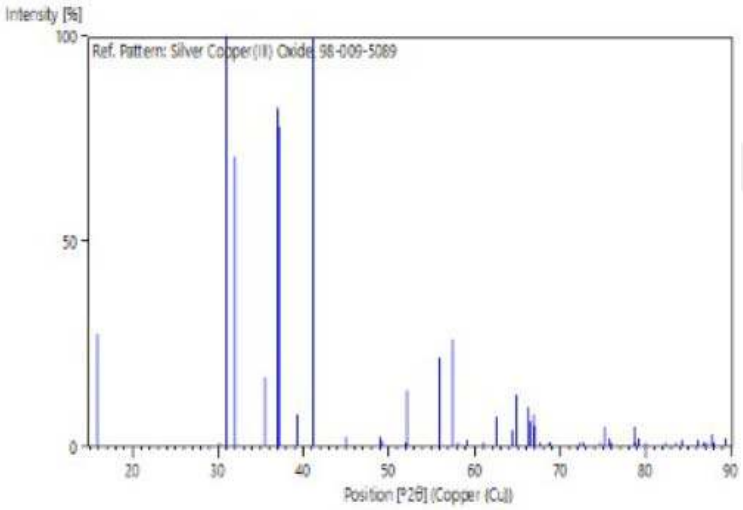


Figure 6.5. XRD results of the catalyst

### 6.1.3. BET Analysis:

BET analysis results are presented in Table 6.1. As shown in Table 6.1, The BET surface area has decreased from 0.67 to 0.583 sq.m/g , possibly due to the calcinations of the catalyst in intense temperatures, the micro pore volume, has also, decreased from 0.11 to 0.03 cub.mm/g which is attributed to the coating

materials on the surface of the catalyst. A slight decrease in Langmuir surface area can also be observed.

Table 6.1. BET analysis results

| | Cordierite | Catalyst |
|---|---|---|
| Micro pore volume[cub.mm/g] | 0.11 | **0.03** |
| Bet Surface area[sq.m/g] | 0.67 | **0.583** |
| Langmuir surface area[sq.m/g] | 0.94 | **0.91** |

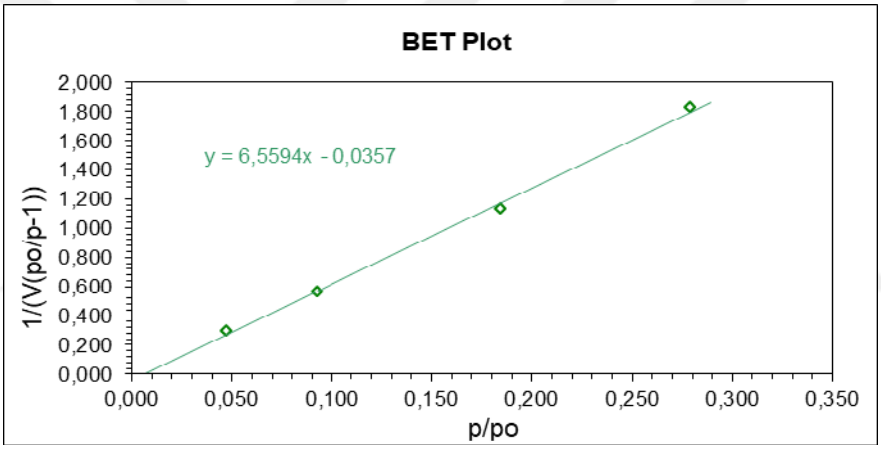


Figure 6.6. Cordierite BET plot

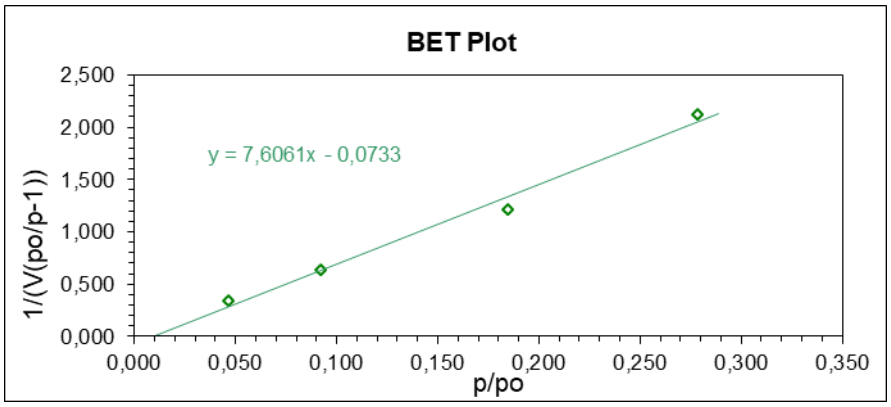


Figure 6.7. Catalyst BET plot

**6.2. Emissions measurement of Diesel engine results:**

Table 6.2. Emissions measurement results

| Emissions/Loads | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| O2(%) | 15.75 | 14.93 | 14.14 | 13.73 | 13.47 | 13.05 | 12.78 | 12.33 |
| CO2(%) | 3.65 | 4.27 | 4.88 | 5.11 | 5.44 | 5.73 | 5.9 | 6.37 |
| CO(%) | 0.061 | 0.048 | 0.039 | 0.033 | 0.032 | 0.033 | 0.035 | 0.04 |
| NO(ppm) | 175 | 247 | 327 | 371 | 366 | 363 | 329 | 311 |
| NOx(ppm) | 184 | 263 | 344 | 387 | 380 | 375 | 338 | 319 |
| NO2(ppm) | 9 | 16 | 17 | 16 | 14 | 12 | 9 | 8 |
| SO2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Propane | 117 | 116 | 114 | 114 | 115 | 114 | 115 | 113 |
| Hexane | 64 | 64 | 63 | 63 | 63 | 63 | 63 | 62 |
| CxHy | 64 | 64 | 63 | 63 | 63 | 63 | 63 | 62 |
| K(1/m) | 0.049 | 0.051 | 0.056 | 0.066 | 0.148 | 0.171 | 0.273 | 0.388 |
| N(%) | 2.1 | 2.2 | 2.4 | 2.8 | 6.2 | 7.1 | 11.3 | 15.3 |

Table 6.2 shows the various emissions of a diesel engine and their rates with a diesel engine working in normal conditions and progressively loaded from 1KW to 7KW.

As can be seen in table 6.2, the loading had different effects on different emissions; the amount of Oxygen $O_2$% has decreased with loading from 15.75% at rest, to 12.33% at loading 7KW. Carbon monoxide $CO_2$%, on the other hand has increased from 3.65% at 0kw loading to 6.37% at 7KW loading. Carbon monoxide CO% almost stayed the same with loading; Nitrogen Oxides (NO) amount (ppm) started with 175 ppm at rest, and peaked at loading=3KW and then decreased gradually with loading (311ppm at 7KW). NOx rate was highest at loading=4KW (380ppm) and lowest at rest (184ppm); $NO_2$ (ppm) reached its maximum at loading=2KW with 17ppm and lowest rate at loading=7KW. For emissions like propane, Hexane, and hydrocarbons (CxHy), their amounts stayed almost the same with loading. It was concluded that loading a diesel engine causes an increase in NOx and NO emissions rates particularly and has not much of an effect on the other emissions rate.

**6.3. NOx Conversion rates:**

In this section, the results of the test engine experiments with Ag-Cu as a catalyst and Ethanol as a reductant and its effects on the NOx conversion rates were discussed according to temperature, loading, spraying ratios, and space velocity. In the experiments, the NOx conversion rates were measured in four different loads (1KW,2KW,3KW,and 4KW), two different space velocities (20000$h^{-1}$,40,000$h^{-1}$), temperature range of(170-260°C), and with different distilled water to ethanol ratio (4:96, 8:92; 0:100).

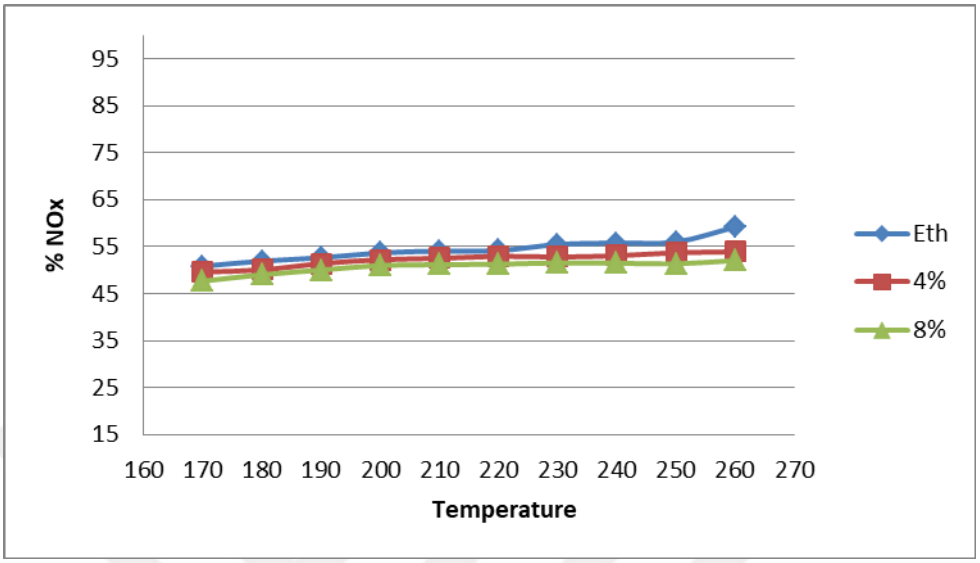


Figure 6.8. NOx conversion rates at 40000$h^{-1}$/1KW

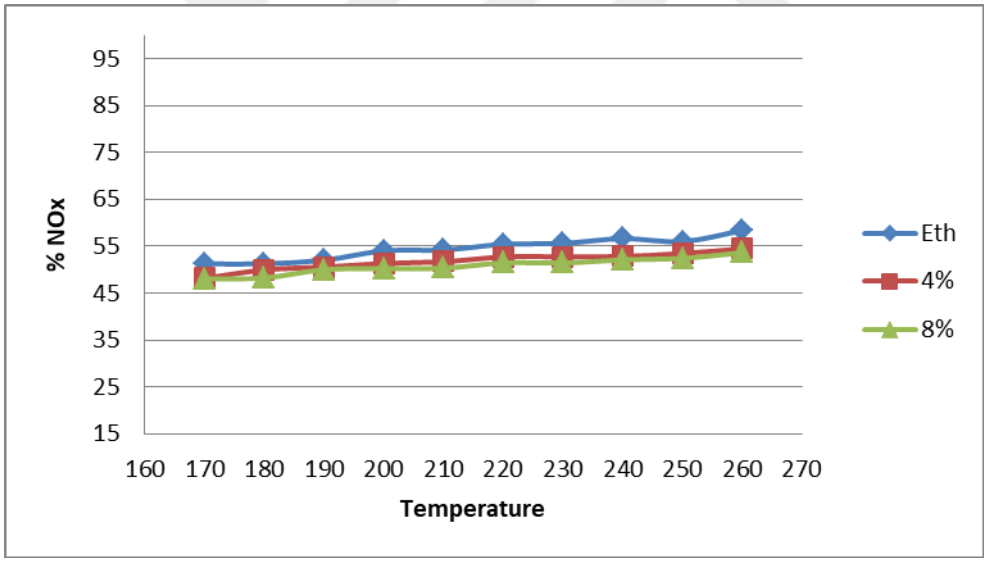


Figure 6.9. NOx conversion rates at 40000$h^{-1}$/2KW

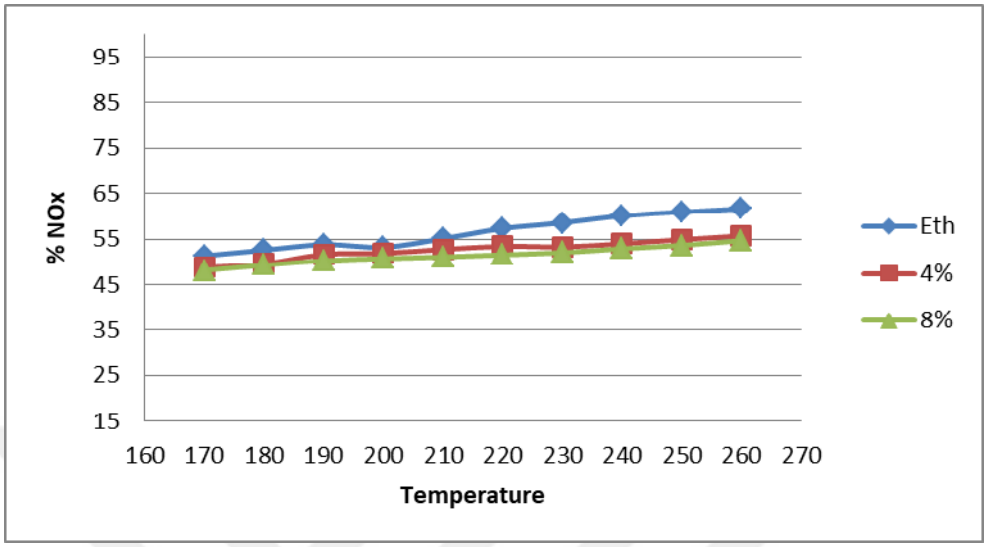


Figure 6. 10. NOx conversion rates at 3KW/40000h$^{-1}$

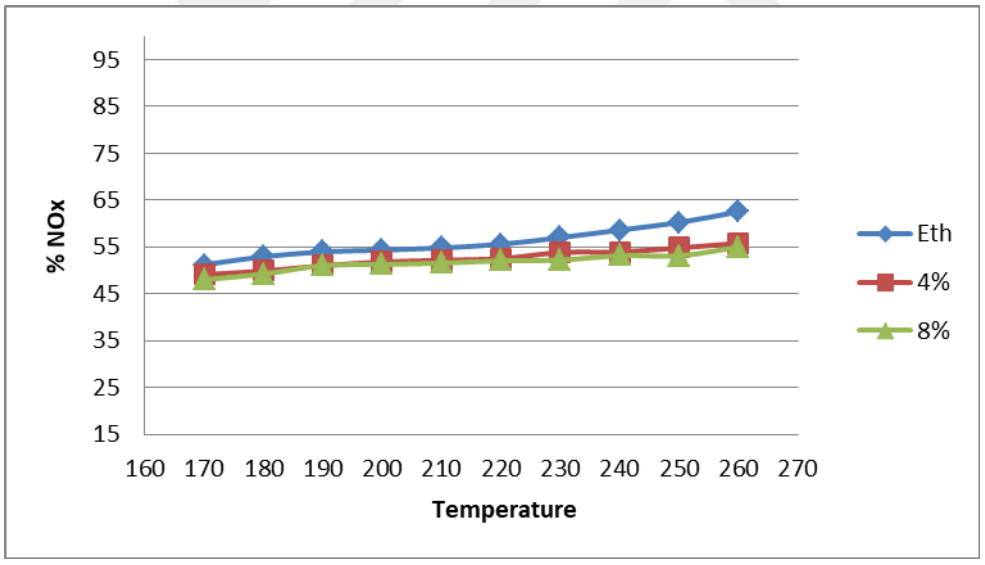


Figure 6.11. NOx conversion rates at 40000h$^{-1}$/4KW

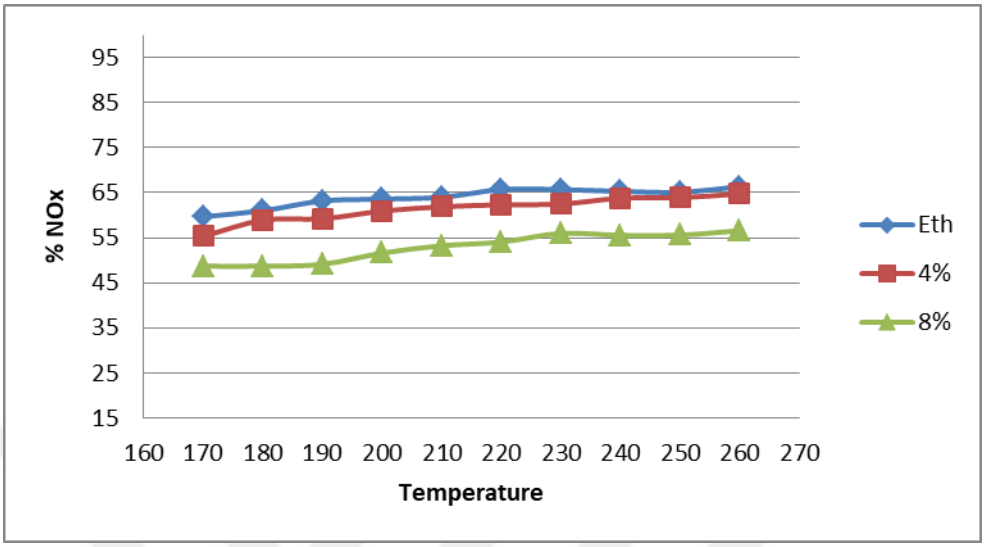


Figure 6.13. NOx conversion rates at 20000h$^{-1}$/1Kwh

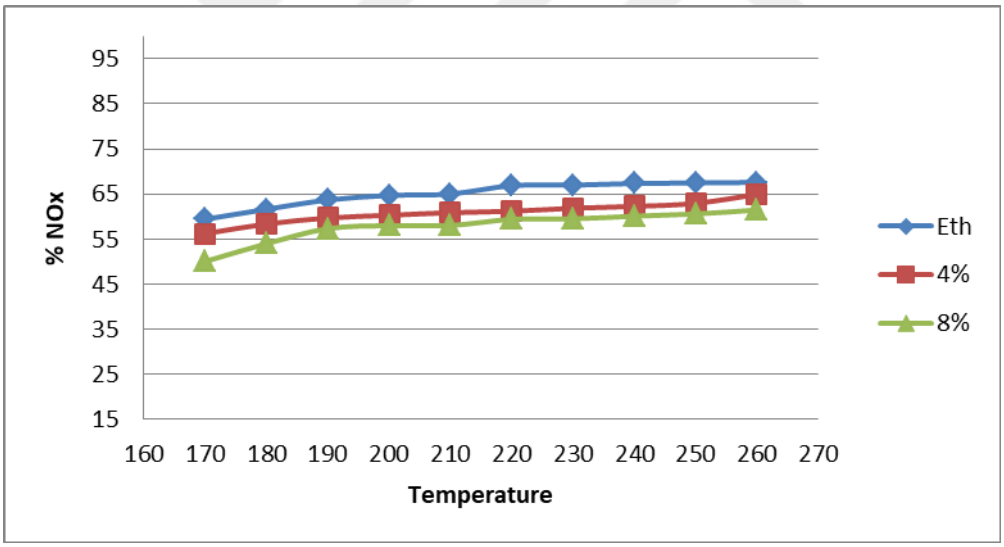


Figure 6.12. NOx conversion rates at 20000h$^{-1}$/2KW

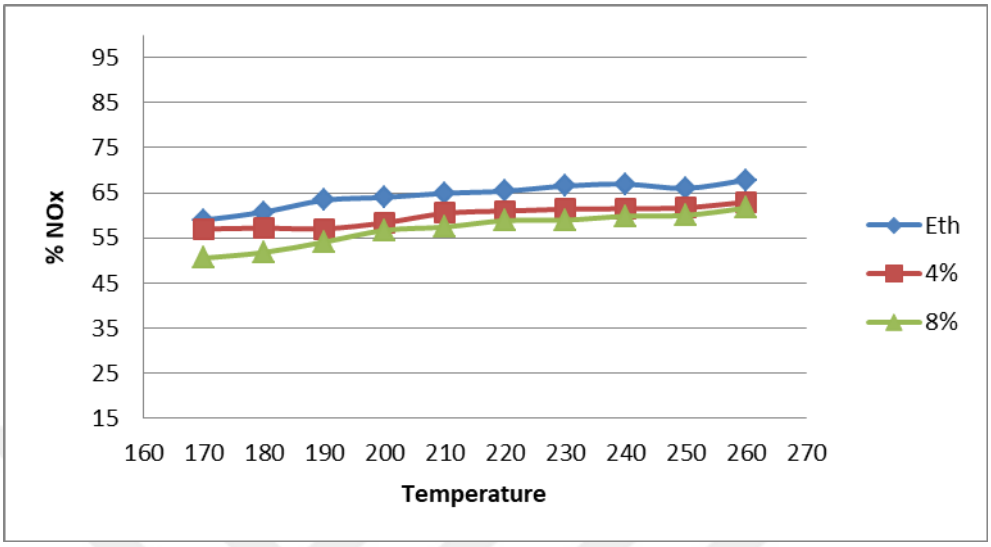


Figure 6.14. NOx conversion rates at 20000h$^{-1}$/3KW

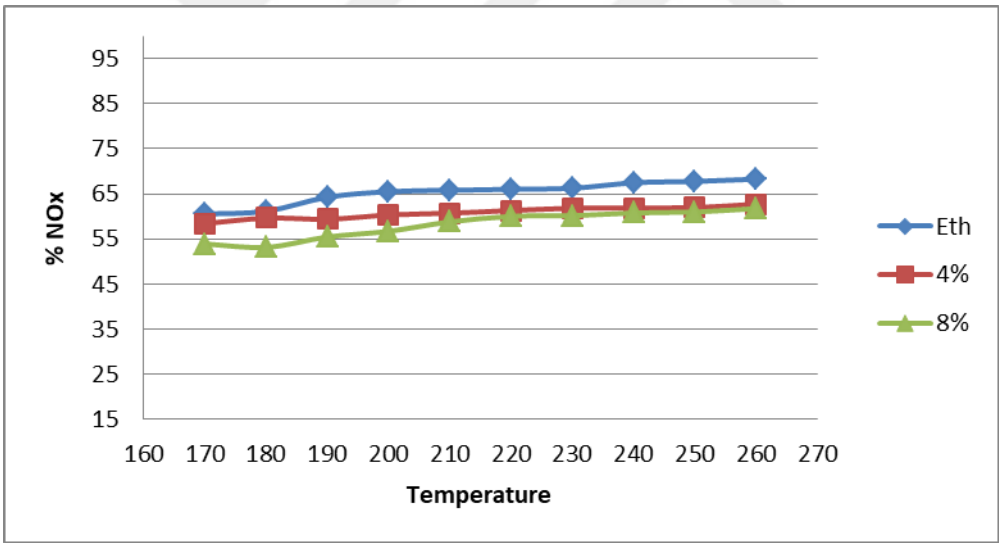


Figure 6.15. NOx conversion rates at 20000h$^{-1}$/ 4KW

### 6.3.1. Temperature effect:

According to Figure 6.8, the NOx conversion rates at SV=40000$h^{-1}$ ,engine load=1KW, exhibited a constant rise of NOx conversion rates at three different reductant spraying ration starting with 46 % at 170°C and peaking at 55% ,56%,and 62% for the three trends. In Figure 6.9 (40,000$h^{-1}$/3KW), NOx conversion rates showed also an increase from 46% peaking at 58% with slight fluctuations along the trends. Figure 6.10 also showed similar trends of NOx conversion rates starting at 46% and peaking at 63% except for a slight decrease at T=200 °C. Figure 6.11 also showed similar trends of NOx conversions following a linear increase till approximately 64% at 260. At a SV=20000$h^{-1}$/s. Figure 6.12,Figure 6.13,Figure 6.14,and Figure 6.15 showed increasing in NOx conversion rates along with Temperature increase, with a peak conversion rates of 66%,67%,and 68% respectively for Figure 6.8,Figure 6.9,Figure 6.10, and Figure 6.11 at T=260°C. In conclusion, the temperature had a proportional effect on the NOx conversion rates; whenever the temperature increased, the increase of the NOx conversion rates followed.

### 6.3.2. Space Velocity Effects:

Graphs with space velocity=20000$h^{-1}$ were compared to the graphs with space velocity=40000$h^{-1}$. It was shown that at SV=20000$h^{-1}$, conversion rates had started between 46% and 56% at T=170°C and peaked at temperatures between 56% and 67% , Whereas, at SV=40000$h^{-1}$, NOx conversion rates kicked off with temperatures ranging from 46% to 50% at T=170°C, and reached maximum temperatures ranging from 54% to 63% at T=260°C. The analysis of the graph taking into account the space velocity, showed that the experiments done with SV=20000$h^{-1}$ showed better conversion rates that with SV=40000$h^{-1}$. SV values are proportional to the exhaust gas flow ratios; this is why, the increase in gas flow causes NOx conversion rates to plummet, because in a unit time, the amount of NOx that must be converted goes up with the exhaust gas flow ratios' increase.

### 6.3.3. Spraying ratios effects:

The analysis of Graph 1 (Figure 6.8) to 4 (Figure 6.11), taking into account the spraying ratios showed almost similar trends of NOx conversion rates including a minor bumps along the way, for example at T=200°C when the conversion rate dropped 1 percent(Figure 6.9) , and sometimes exhibited a plateau for a while like between T=200°C and T=215°C when NOx conversion rate kept constant at 55% (Figure 6.11) but other than that the trends were almost similar with a spraying ratio of 100% Ethanol (blue trends), conversion rates ranged between 51 to approximately a maximum of 68% conversion rate at T=260 (Figure 6.9). For a Spraying rations with 96% Ethanol and 4% distilled water (pink trends), conversion rates lurched between 46% and a maximum of 65% at T=260 (Figure 6.9). Spraying with 92% Ethanol, and 8% distilled water (green trends), the conversion rates ranged between 46% and peaked at a maximum of 62 %(Figure 6.10). It was inferred from the results that distilled water mixing with ethanol had negative effects on the performance of the catalyst and thus lower conversion rates were obtained.

### 6.3.4. Engine loading effects:

At SV=20000$h^{-1}$, The Loading of the engine from 1KW to 4KW had caused only a few point of increase in the NOx conversion rates at temperatures between 230°C and 250°C (figure 6.9) for the blue trend with 66% maximum at 4kwh as opposed to 65% at 1KW,caused a slight decrease in conversion trends, especially at T=260°C where NOx conversion rates decrease from 65% to 63%(Figure 6.11). For the green trends , NOx conversion rates trends increase with motor loading with a maximum at 4KW of 62% at T=260°C (Figure 6.11). At SV=40000$h^{-1}$, the three NOx conversion rates also exhibited a slight increase with engine loading with a maximum (4KW) of 64% at T=260°C (Figure 6.15). Despite the slight decrease of the pink trend that was witnessed with engine loading in figure 6.11. The overall conclusion is that Loading at 4KW provided the best NOx

conversion results albeit it was close to the results with other loads. The motor loading, generally, had only a slight effect on the performance of the catalyst and the conversion rates of $NO_x$.

### 6.3.5. Maximum Conversion rate recorded:

The maximum NOx conversion rates was approximately 68% rates at SV=$20000^{-1}$, motor loading=4KW, and 100% Ethanol spraying ratio.

## 6.4. Conclusion and recommendations:

### 6.4.1. Conclusion:

The work done in this thesis on the after engine exhaust control system involved a silver-copper catalyst preparation using the impregnation method, To determine the catalyst characteristics, SEM, BET, and XRD analysis were conducted, in the SEM analysis, it was observed that the prepared catalyst had a porous structure, that the coatings of the catalyst spread homogeneously over its surface, and that the coating materials penetrated its surface. In The BET analysis the surface area of the catalyst was determined, and the XRD analysis proved SEM analysis results with the peaks that are thought to represent the coating materials copper and silver, and thus showed the crystal and micro structure of the catalyst. Compared to uncoated catalysts, BET analysis showed a decrease in the surface area of the coated catalyst due to either the sintering of the catalyst, or the penetration of the coating materials to the surface of the catalyst. The catalyst BET surface area was determined to be 0.58sq.m/g for the catalyst which showed a decrease compared to the BET surface are of the cordierite, and this decrease was attributed to the calcinations of the catalyst or the penetration of the coating materials to the surface pores.

To test the prepared catalyst (Ag-Cu) in real time conditions, a specific test performance was installed in the laboratory of automotive engineering department in Cukurova University. The exhaust system consisted of sensors, heater, pump,

electronic control system, computer programs which monitored the NOx flow rates and hydrocarbon spray rate, DOC, and SCR system with all the accompanying components for monitoring and control. This emission exhaust system was installed after the diesel engine and the loading system. The Ag-Cu catalyst was tested with Ethanol as a reductant in various conditions of engine loading (1KW, 2KW, 3KW, and 4KW), Spraying ratios, and two different space velocity ($20000h^{-1}$, and $40000h^{-1}$). The total of the experiments conducted was eight experiments. The results showed that when the temperature increased, the increase of the NOx conversion rates increased too; taking into account the space velocity, the results showed that the experiments done with $SV=20000h^{-1}$ gave better NOx conversion rates that with $SV=40000h^{-1}$; It was also inferred from the results that distilled water mixing with ethanol had negative effects on the performance of the catalyst and thus lower conversion rates were obtained; as for the engine loading, it generally had only a slight effect on the performance of the catalyst and the conversion rates of $NO_x$. The maximum $NO_x$ conversion rate recorded throughout the experiment was 68% rates at $SV=20000^{-1}$, motor loading=4KW, and 100% Ethanol spraying ratio.

### 6.4.2. Recommendations:

In Turkey, the scientific research and development in the field of after engine emissions is limited. This is why any addition to the literature would serve as a push toward getting better solutions to eliminate diesel engines exhaust NOx emissions. The results obtained in this thesis might serve as a reference to future research in after-engine emissions regulations. For future research, different variation can be applied and experimented in order to observe if better conversion rates can be achieved: The coating materials of the catalyst can be changed in amount and ratios; the effect of different spraying ratios can be researched; the effect of different space velocities could be researched; an optimization in the SCR

system can be researched and applied to obtain better NOx conversion rates, experiments might be conducted in various temperature windows.

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